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UNSATURATED CYCLIC KETONES. IV*. THE RELATIVE BASICITIES OF ARYLIDENE DERIVATIVES OF BENZOCYCLOALKANONES AND THEIR HETEROANALOGUES

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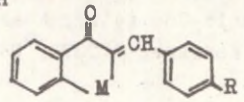
The relative basicities of 1-indanone, benz[b]-furan-3(2H)-one, benz[b]thiophen-3(2H)-one, 1-tetralone, 4-phenyl-1-tetralone, 1-chromanone-4, 1-thiochromanone-4, 1-selenochromanone-4, 1-benzosuberone, 1-homochromanone-5, and 1-thiohomochromanone-5 as well as their arylidene derivatives have been evaluated by IR spectroscopy from the shifts of the stretching frequency of the hydroxy group of phenol participating in hydrogen-bonding with these ketones. All compounds have generally been considered with the common position as analogues to π-systems perturbed by different bridge groups. Such an approach showed that one of the main factors, determining the proton-acceptability of the compounds, is the degree of acoplanarity of their molecules. It was established that the basicities of these ketones decrease if the size of the rings increases. The analogous effect is caused by the introduction of bridge groups, containing heteroatoms, which brings about the reduction of the total polarity of the

* - The preliminary communication is given in [1].

molecules. The conductivity of the electronic influence of the studied π-systems was evaluated and compared.

During recent years a great deal of experimental material on the investigation of the basicities of different cyclic unsaturated ketones has been gathered using IR spectroscopy[2-7] (from the shifts of stretching frequency band of phenol, hydrogen-bonded with carbonyl compounds - $\Delta\nu_{OH}$) . Present paper is the continuation of these researches in which the $\Delta\nu_{OH}$ values of 8 series of compounds with the general formula



(M and R are given in Table 1)

were systematized and studied.

The common feature of the ketones of all these series is the presence of the same π-systems which are identical to chalcones (M is absent). At the same time, unlike the latter existing as a mixture of s-conformers whose proportions depend on the phase conditions of the ketones, temperature and solvents and which are seldom identified, the compounds given in Table 1 are characterized by the fixed s-cis-conformations. This type of object selection permits to remove the factors of indefiniteness of s-conformations and simply solve the problems concerning the effects of substituent R and bridge group M on the properties of the ketones studied.

It is known[8] that the croton condensation like any other method of synthesis of aromatic α, β -unsaturated ketones. with the participation of acid or alkaline catalyst* is a stereospecific reaction and leads to the formation of exclusively trans-conjugated systems. In reactions of cycloalkanones and their heteroanalogues with aromatic aldehydes,

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* - In the recently published paper[9] it was reported about trans-cis-isomerization of chalcone in the presence of polyphosphoric acid. The abnormality of this fact is obvious. Therefore, in our laboratory the conditions of experiment which is described in[9] were repeated. In every case unchangeable trans-chalcone was restored.

this stereospecificity should stipulate the formation of E-isomers*.

In the works[2,10] attention has been paid to the fact that the E-isomers of the compounds belonging to the I,III, V, and VIII sets have sufficiently intensive and characteristic bands of out-of-plane deformational frequencies of β-CH bonds in the IR spectra. Analogous bands appear in the spectra of ketones of other series (IV - 964-972, VI - 965-970, VII - 957-966, IX - 975-984, X - 945-952 cm^{-1}), which correspond to the trans-configuration of their cinnamal fragment (Independently, this fact is confirmed by the measured values of dipole moments).

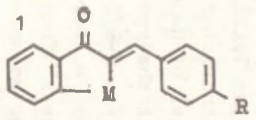
In the present paper the selection of $\Delta\nu_{OH}$ values as the main characteristic of H-complexes which are formed by the studied ketones with phenol, was caused as it was shown in the recent review[11], that especially the $\Delta\nu_{OH}$ values that characterize the strength of separate hydrogenbridge, are slightly dependent on the proportion of the components and, on the contrary, are highly sensitive to the structural changes in these components. That is why its use as the measure of proton-acceptance of ketones is more justified than the use of the association constant values, as in our experiment condition the latter characteristics would show "gross-effect" including the strength of H-complex as well as its interaction energy with the molecules of bases, taken in excess. In our opinion, the indefiniteness of the latter effect makes the values of association constants, determined in excess bases, less effective general characteristics in comparison with those of $\Delta\nu_{OH}$.

The analysis of obtained $\Delta\nu_{OH}$ values (Table 1) allows to note two common tendencies. First of all, in every group of ketones (i.e. different bridges M) the changing of the basicity of compounds is complicated and not similar in differe-

* - In the case of 2-arylidenederivatives benz[b]furan-3(2H)--one (M=O), benz[b]thiophene-3(2H)-one (M=S) and 1-selenochromanone-4 ($M=SeCH_2$) the same trans-configuration of cinnamal fragment should be designated as Z-isomer.

Table 1

The $\Delta\nu_{OH}$ Values of Phenol Associated With Ketones Having General Formula:



N group	N set / M / R	I	II	III	IV	V	VI	VII	VIII	IX	X
	M	CH_2	S	$(CH_2)_2$	$CHRh-CH_2$	OCH_2	SCH_2	$SeCH_2$	$(CH_2)_3$	$O(CH_2)_2$	$S(CH_2)_2$
a	-*	224	170	210	-	192	181[t]	164	205	199	199
b	$N(CH_3)_2$	308	227	251	233	252	210	201	232	204	199
c	OCH_3	268	188	228	208	222	188	181	208	193	187
d	CH_3	258	185	210	192	208	184	176	204	187	184
e**	H	256	180	210	192	198	182[s]	174	202	185	178[i]
f	Cl	239	182	205	190	188	166	172	190	180	175
g	meta-Cl	240	-	197	-	-	-	-	-	-	-
h	Br	240	163	198	-	181	169	177	-	183	178
i	NO_2	130	139	141	159	129	146	161	160	151	154

* - Bicycles in which =CH-⟨⟩-R group is absent have been investigated.

** - The value $\Delta\nu_{OH}$ for 2-benzylidenebenz [b] - furan - 3(2H) - one with M = O is 253cm^{-1}.

t, s, i - S-Dioxides of these compounds have the following $\Delta\nu_{OH}$ values: 119, 128 and 122cm^{-1}, respectivly.

ent groups. Secondly, to every series of compounds (different R) corresponds the linear dependence between the values of $\Delta\nu_{OH}$ and electronic properties of R.

The first particularity will be pointed out and its discussion will be started with the "a" group. For benzocycloalkanone (Ia, IIIa, VIIIa) the $\Delta\nu_{OH}$ values decrease if the size of hydrocycles is extended. This regularity shows, in our opinion, that with the increase of the cycle size its acoplanarity is intensified. It is accompanied by the withdrawal of C=O group from the plane of conjugated benzene nucleous and as a result of weakening of interaction with it. Really, by the opinion[12] it follows from UV spectral characteristics of 1-indanone (Ia), 1-tetralone (IIIa) and 1-benzosuberone (VIIIa) that the C=O group forms a two-dimensional angle Q (with benzene ring) which equals 17, 22 and 39°, respectively. The evaluation of the conformation, taken in paper[12], is rather approximate, which is proved by the alternative angle Q=34° for 1-tetralone, but it seems to indicate the changes in this group of ketones correctly.

The intensification of molecular acoplanarity should have been observed in transition from Va to IXa and from Ha to VIa and Xa. At the same time the minimum values of $\Delta\nu_{OH}$ are observed in the derivatives of six-membered hydrogenated cycles (Table 1). Moreover, the basicity of the bicycles with the heteroatoms of O and S is lower than their hydrocarbon analogues, though the heteroatoms that are in orthoposition to the C=O group must exert electrondonating influence on it. As the analogous phenomena are observed in other groups of compounds., their probable causes will be discussed below.

The introduction of benzylidene radical(compounds of "e" group) remarkably changes the conformation of bicycles in connection with the appearance of a new sp^2-center in it. According to the data of X-ray structural analysis[13] this bicycle is practically flattened in the Ie molecule (it has conversional conformation in the molecule of Ia). The increase of cyclic tension in such flatenning is accompanied by a remarkable deviation of valent angle from normal ones. Thus, the internal angle, attached to C=O group, is 107.2°. This value

determines essential rehybridization of its (C=O) carbon atom, the intensification of its polarity (which shows the increasing values of dipole moments of Ie, Table 2). These effects are supplemented by the electron-donating influence of benzylidene radical which determines the considerable increase of $\Delta\nu_{OH}$ values by transition from Ia to Ie.

The analogous derivation in the series of benz[b]thiophene-3(2H)-one (II), is accompanied by the smallest increase of the $\Delta\nu_{OH}$ values, which, probably, reflects conformational (as a result of greater atomic radius of sulphur) rearrangements of bicycle.

In molecules with a bicycle which contains a six-member hydrogenated ring, appearance of benzilidene radical should ever favour the flattening of benzoyl fragment. Thus, according to the available data presented in[14] the acoplanarity of bicycle in 2-benzilidene-1-tetralone (IIIe) is caused by the withdrawal of CH_2 group out of the plane of the aromatic ring (dihedral angle between C_6H_4 and C-CH_2-C fragments is 136.2°). As regards the C=O group, it is withdrawn out of the plane of the annulated benzene ring at an angle of 11.8°, i.e. considerably less than that of the 1-tetralone itself (22°). The angles under comparison are determined for different aggregative states of molecules, but sufficiently rigid structure of bicycle allows to assume that the variation of these parameters will not be great during dissolving of these substances. The bicycling flattening was noted when UV spectra of Va-VIIa and Ve-VIIe were considered[15].

It was to be expected that the effect of benzoyl fragment, flattening which was mentioned above, would have promoted the increment of basicity. Such a tendency is weakly displayed in compounds Ve-VIIe. But, probably, it reflects the fact that the endo-heteroatom which conjugated with C=O group, in consequence of its influence on basicity increases when bicyclic system is flattened. At the same time benizilidene radical creates some kind of a screen to the carbonyl group, that should adversely affect its H-complex--formation with bulky molecule of phenol. The complex of

Table 2

The Values of $\nu_{C=O}$ (cm^{-1}, CCl_4), Dipole Moments (μ in D, benzene, 25°C), Integral Intensities ($I_{C=O} \cdot 10^4$ mole · l · cm^{-1}, CCl_4) and $\Delta\nu_{OH}$ (cm^{-1})

Group	Set / Property	I	II	III	V	VI	VII	VIII	IX	X
"a"	$\nu_{C=O}$	1725	1705	1695	1693	1692	1682	1685	1689	1689
	μ	3.30	2.18	3.01	2.19	2.06	2.07	-	2.28	1.64
	$\Delta\nu_{OH}$	224	170	210	192	181	164	205	199	199
"e"	$\nu_{C=O}$	1704	1685	1679	1677	1670	1668	1673	1678	1678
	μ	3.52	2.41	3.21	2.71	2.32	2.14	2.91	3.07	3.41
	$I_{C=O}$	1.43	1.12	0.50	1.28	0.85	0.72	0.95	0.60	0.84
	$\Delta\nu_{OH}$	256	180	210	198	182	174	202	186	178

these factors determines the character of changing of $\Delta\nu_{OH}$ values.

Analyzing $\Delta\nu_{OH}$ values of seven-membered ring ketones, we can come to the conclusion that the steric hindrances created by benzilidene radical act as the dominating factor in reduction of the basicity of these compounds.

Introduction of heteroatom to the bicycle of the compounds of "e" group as well as "a" group, independent of the sizes of heterocycles, decreases the basicity. As the heteroatom is conjugated with the C=O group the reciprocal effect would have been expected. Any specific interaction of phenol with heteroatoms was not observed. The spectral curves of benzocycloalkanone derivatives and their heteroanalogues are similar. Besides, in the compounds of "b" and "c" groups whose substituent R contains the same number of basic heteroatoms, their interaction with phenol was not observed. In the compounds of "a" and "e" groups the direct dependence between the values of $\Delta\nu_{OH}$, $\nu_{C=O}$, $I_{C=O}$ and μ is absent

(Table 2). Here it reflects complicated relations between electronic and conformational effects, acting in the investigated molecules and displaying their properties in different ways. Supposedly the polarization of the C=O group and the total polarity of the ketone molecules playing a significant role in their H-association with phenol are overlapped by such factors, as steric hindrance of complex formation, or conformational rearrangement of bicyclic system caused by the M bridge groups of different size and electronic nature.

In the note to Table 1 the $\Delta\nu_{OH}$ values of dioxides of sulphur-containing compounds are given. It is clear that a sudden intensification of electrondonating properties of bridge group M observed at oxidation of S to SO_2 is accompanied by a quick decrease of basicity. In this case the electronic effects of bridge M clearly dominate over the conformational ones.

In order to determine the conductivity of electronic effect in molecules I-X, the correlation analysis of $\Delta\nu_{OH}$ values was carried out by means of one-parameter equations 1 and 2 with σ-(Brown's constants[16]) and σ°-parameters as well as the Yukawa-Tsuno's two-parameter equation 3(σ°- and σ_R^+-parameters were taken from[17]).

The obtained results, first of all, prove that the best description of electron properties of α, ß-unsaturated ketones investigated is achieved by using equations 1 and 3, which take into consideration not only the inductive effect, but also the resonance effect of substituent R. It should be noted that the sensitivity of the $\Delta\nu_{OH}$ values of the effect of substituent R, which was observed in compounds of different series, is reflected by equations 1 and 3 practically the same way. According to the character of changes of parameters m, m_o, A, and B the investigated series of compounds may be represented by the following sequence: V > I > II > III ≈ IV > VI ≈ VIII > VII ≈ IX ≈ X. The main factor determining this sequence, in our opinion, is the degree of acoplanarity of cinnamoyl fragment in the molecules of different sets. The

Table 3

The Parameters of Correlations 1-3

Equation 1: $\Delta\nu_{OH} = m\sigma + c$

№ set	X	m	c	c.c.*	s_o§	n t
I	CH_2	-59	254	0.98	5	7
II	S	-50	181	0.94	5	6
III	CH_2CH_2	-46.5	210	0.99	3	7
IV	$CHPhCH_2$	-45	195	0.99	3	6
V	O-CH_2	-65	199	0.99	4	6
VI	S-CH_2	-39	180	0.99	3	6
VII	Se-CH_2	-25	177	0.92	3	6
VIII	$CH_2CH_2CH_2$	-44	197	0.99	3	6
IX	O-CH_2CH_2	-20	186	0.98	3	6
X	S-CH_2CH_2	-22	177	0.98	3	6

Equation 2: $\Delta\nu_{OH} = m^{o}\sigma^{o} + c$

№ set	X	m	c	c.c.	s_o	n
I	CH_2	-51	256	0.97	7	7
II	S	-61	187	0.93	6	7
III	CH_2CH_2	-89	211	0.95	6	7
IV	$CHPhCH_2$	-54	200	0.89	8	6
V	O-CH_2	-93	206	0.96	7	7
VI	S-CH_2	-43	180	0.98	2	7
VII	Se-CH_2	-26	180	0.87	6	7
VIII	$CH_2CH_2CH_2$	-54	203	0.93	4	6
IX	O-CH_2CH_2	-39	187	0.95	5	7
X	S-CH_2CH_2	-33	182	0.96	4	7

* - Correlation coefficient.

§ - Total dispertion.

t - Number of points for correlation.

The compounds with the maximum electronic conductivity - the derivatives of 1-chromanone-4 (V), 1-indanone (I) and

Equation 3: $\Delta\nu_{OH} = A\sigma^{o} + B\sigma_{R}^{+} + C$

N set	M	A	B	C	C.c.	S_o	S_A	S_B	n
I	CH_2	-44	-23	251	0.93	6	14	8	7
II	S	-31	-24	177	0.94	10	25	13	6
III	CH_2CH_2	-34	-18	210	0.99	1	2	1	6
IV	$CHPhCH_2$	-39	-16	193	0.98	3	5	4	6
V	$O-CH_2$	-82	-13	198	0.99	4	6	5	6
VI	$S-CH_2$	-42	-8	178	0.99	3	7	4	6
VII	$Se-CH_2$	-4	-17	172	0.96	4	10	5	6
VIII	$CH_2CH_2CH_2$	-40	-9	199	0.99	4	13	6	5
IX	$O-CH_2CH_2$	-14	-9	184	0.99	2	4	2	6
X	$S-CH_2CH_2$	-15	-9	179	0.99	2	5	2	6

benz[b]furan-3(2H)-one (III) - have practically flattened structure. Later on, acoplanarity of the cinnamoyl fragment is intensified periodically, first of all, by the increase of the acoplanarity of the hydrogenated cycle, which is connected with the cinnamoyl fragment.

The authors of the communication[18] for 2-aryliden-4-phenyl-1-tetralones (IV) have succeeded in proving that the increase of electrondonating properties of R substituent does not bring about only the increase of its conjugation with carbonyl group, but at the same time cinnamoyl fragment and the bicycle conjugated with it flatten out. This peculiarity of conjugated systems can be controlled by the change of the vicinal constants of spin-spin interaction (J) of the $CUPhCH_2$ bridge-group protons. It turned out that in this set of compounds, R = NO_2 substitution for $R=N(CH_3)_2$ is accompanied by the change of dihedral angle in the $CHPhCH_2$ group to 10-20°. Unfortunately, this approach of conjugated molecules conformational behavior analysis can have limited use only. Thus, the bridge groups of the compounds of I, II,

V-VII sets have no vicinal protons, and in the molecules of the compounds belonging to the other sets a rapid (in NMR time scale) invertability of partly hydrogenated cycle is observed. that results in the averaging of the constants.At the same time it is obvious that the phenomenon itself - the changing of conformation of cinnamoyl fragment (or more exactly, the changing of its aooplanarity degree), if there are variations of R, is of general character. This means that the m, m_o, A, and B partly include this lability factor of the conjugated system of bonds.

Experimental

The data on the $\Delta\nu_{OH}$ values of the majority of the compounds belonging to I, III, V and VIII sets are represented in [2,4]; the measuring of these values for the rest of ketones was carried out similarly: in the system CCl_4 - ketone (0.06 - 0.1 mole/l) - phenol (0.02 mole/l), A spectrometer UR-20 (prism - LiF, cell thickness 1 mm). The confidencial range of the $\Delta\nu_{OH}$ values is $\pm$ 2-3 cm^{-1} (confidence level 0.95). The correlation parameters were calculated using the least squares method at a computer ECM. The calculations. for equations 2 and 3 have been done by prof. V.A. Palm according to his programs, and the authors are grateful to prof. V.A. Palm for his assistance.

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PROGRAM PACKAGE FOR COMPUTER STORAGE AND AUTOMATIC SEARCH OF CORRELATION EQUATIONS AND FOR CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS. 2. ALGORITHM FOR SEARCH OF INDEX OF CORRELATION EQUATION FROM IDENTIFICATION ARRAYS ON THE BASIS OF REACTION AND SUBSTITUENT CODES.

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The algorithm for the search of reaction sets on the basis of digital reaction and substituent codes has been presented. The search includes the comparison of ordered reaction and substituent codes with those inserted into the information arrays of the program.

In the previous paper of this series[1] the digital coding system of the equations of chemical reactions accepted in our program package has been described. The most "chemical" part of the program of the search of correlation equations, the search of the correlation equation index on the basis of reaction and substituent codes rests on this system.

The search begins with the determination of the reaction type index /RTI/ by means of a direct comparison of the ordered reaction code /ORC/ (for the mode of coding see paragraph 3 in Ref. 1) with items of the two-dimensional array of reaction codes /ARC/. If the ordered code does not coincide with the items of the ARC, the "inversion" of the ordered code is carried out, i.e. the codes of the first nucleophile and electrophile are replaced by the second ones and vice versa, and the comparison is repeated. If the coincidence takes place, the comparison of ordered codes of var-

iable substituents /CVS/ (for the mode of coding see paragraph 5 in Ref. 1) with the corresponding elements of identification arrays /IA/ follows after dividing up the ordered reaction code to the codes of structural units (electrophiles and nucleophiles) and determining of the number and the equivalence indexes of the variable substituents in structural units.

The identification arrays are organized as one-dimensional arrays with complementary arrays of base addresses. Such a system quarantees, on the one hand, the compactness of arrays, on the other hand - the possibility of the compilation of an uncomplicated system for adding new codes to them.The mode of the substituent coding in identification arrays has been described in paragraph 4 in Ref. 1. Making use of base addresses as well as of the substituent's code structure,the identification arrays could conventionally be divided into the arrangements of items corresponding to the bridge and secondary substituent codes of one substituent.Ordered codes of variable substituents are put into a two-dimensional array ACVS, every line of which corresponds to one substituent. Thus, the comparison of one code of a variable substituent and the corresponding elements of identification array means the comparison of a line of the ACVS array with a "line" of identification array, if the code of a variable substituent corresponds to the substituent in an inequivalent (if compared with other substituents) position. If the code of a variable substituent corresponds to the substituent in one of the N equivalent positions, the line of the ACVS array is to be compared, depending on the result of every separate act of comparison, with one to N "lines" of the identification array.

Every separate comparison as well as the total comparison cycle has three possible results:

- total coincidence of codes, i.e. the ordered substituent was the same that was coded in the identification array;
- "connectivity" of the ordered code to that of the identification array. The latter result is possible in case there is the code of variable secondary substituent /VSS/ among

the codes of secondary substituents /CSS/ of the identification array (see paragraph 4 in Ref. 1.). It is checked up in such a case if the ordered code of variable substituent satisfies the requirements which allow the calculation of numerical characteristics (substituent constants - SC) for the ordered substituent according to the type of variable substituent in the identification array;

- the lack of the coincidence or the "connectivity". In the case of the pairwise coincidence of all the lines of the ACVS array with the "lines" of the identification array (i.e. the pairwise coincidence of all substituent codes of the order and the identification array) or the pairwise coincidence of all "lines" of the identification array without variable secondary substituents with the same number of the order lines and the pairwise connectivity of all other ordered substituents to the substituents of the identification array with the variable secondary substituent, the index of reaction set is equal to the index of the item of the corresponding reaction set in the array of base addresses. By a positive result, this index as well as the content of the array with the connectivity information is the main result of the functioning of the segments of the program package which calls for the reaction set search. If there were connected substituents, these activities would be followed by the check-up of the possibilities for the calculation of substituent constants and finding the rule code for these calculations. After that, the further subroutines will bring the search of correlation equations (the search of correlation equations with regard to solvent and temperature) to the end.

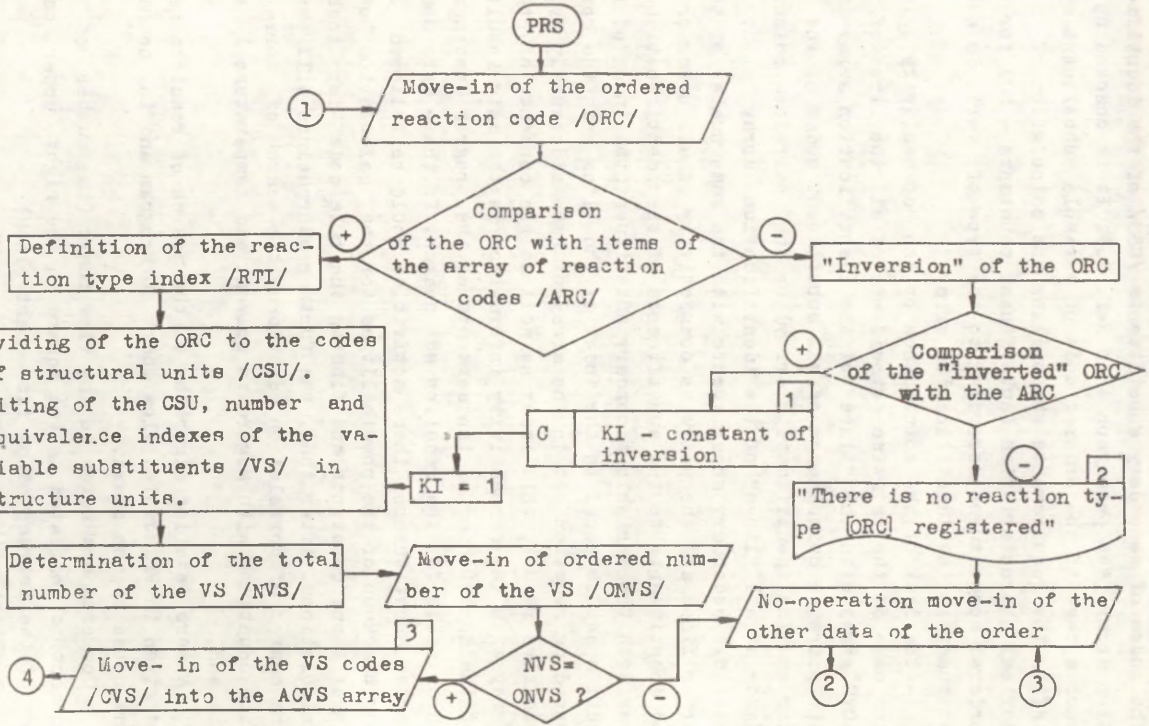
A more detailed algorithm of the search of reaction set is given in Principled Flow Chart of Program and in comments and notes to the chart.

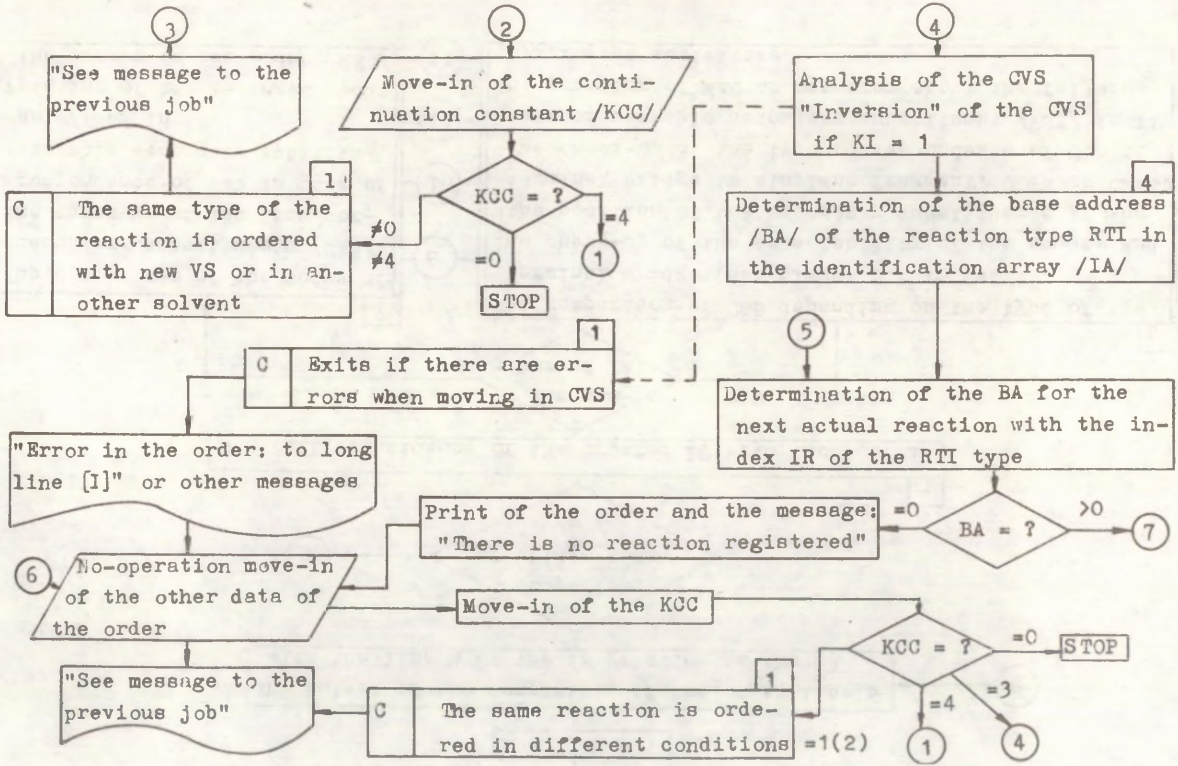
Comments and notes to the flow chart (the number of a comment is indicated in the square in the right upper corner of the corresponding flow chart block):

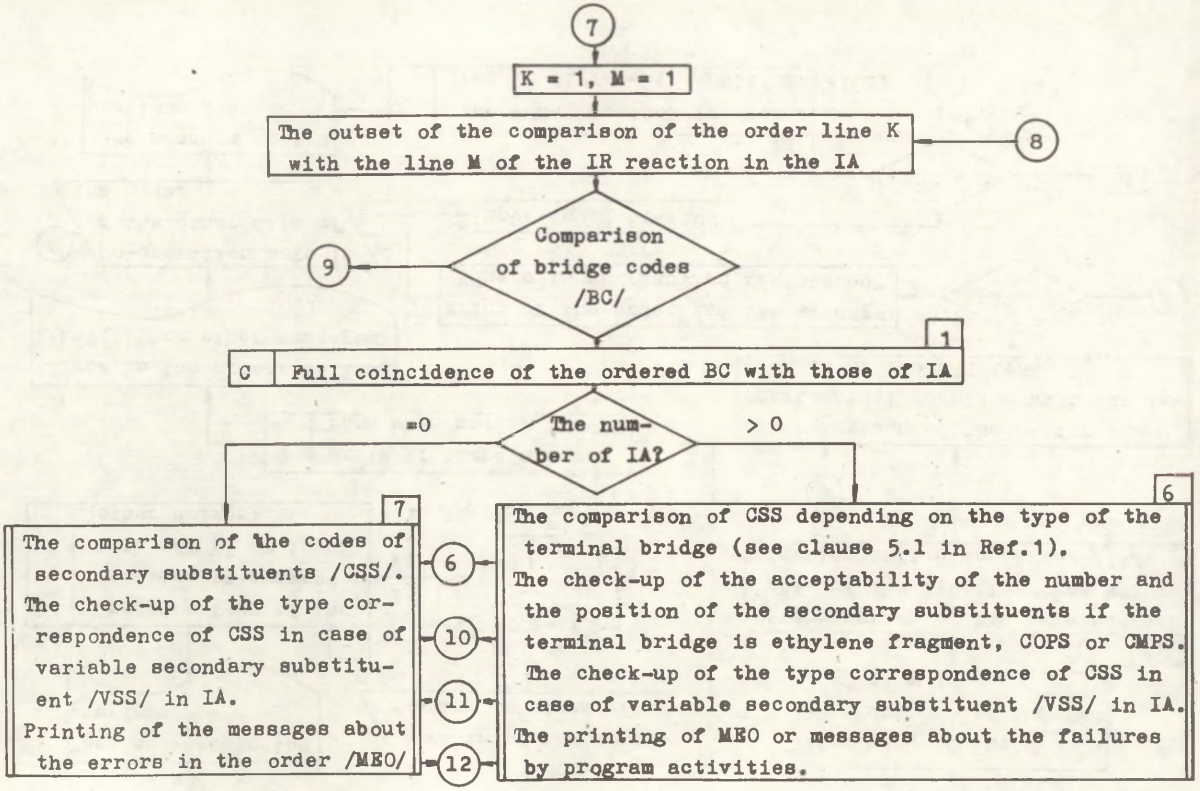
1. Block with comments.

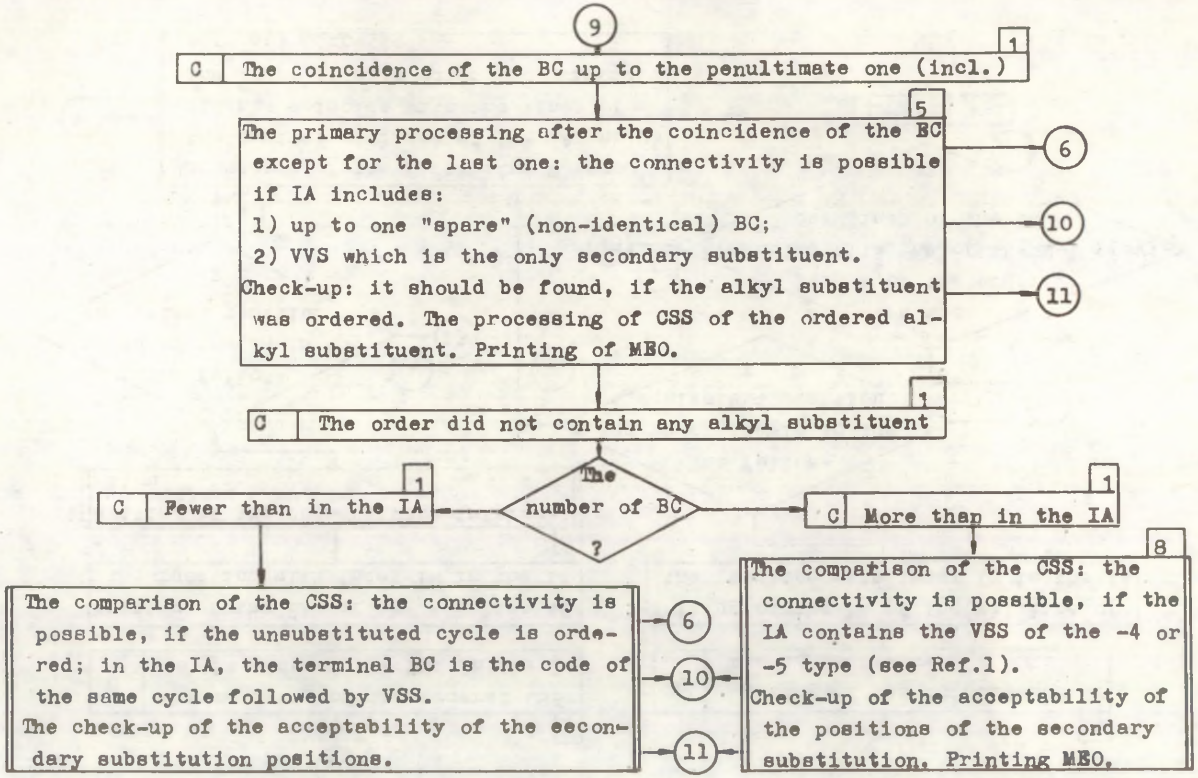
2. Metasymbols for each case are given in brackets. Ac-

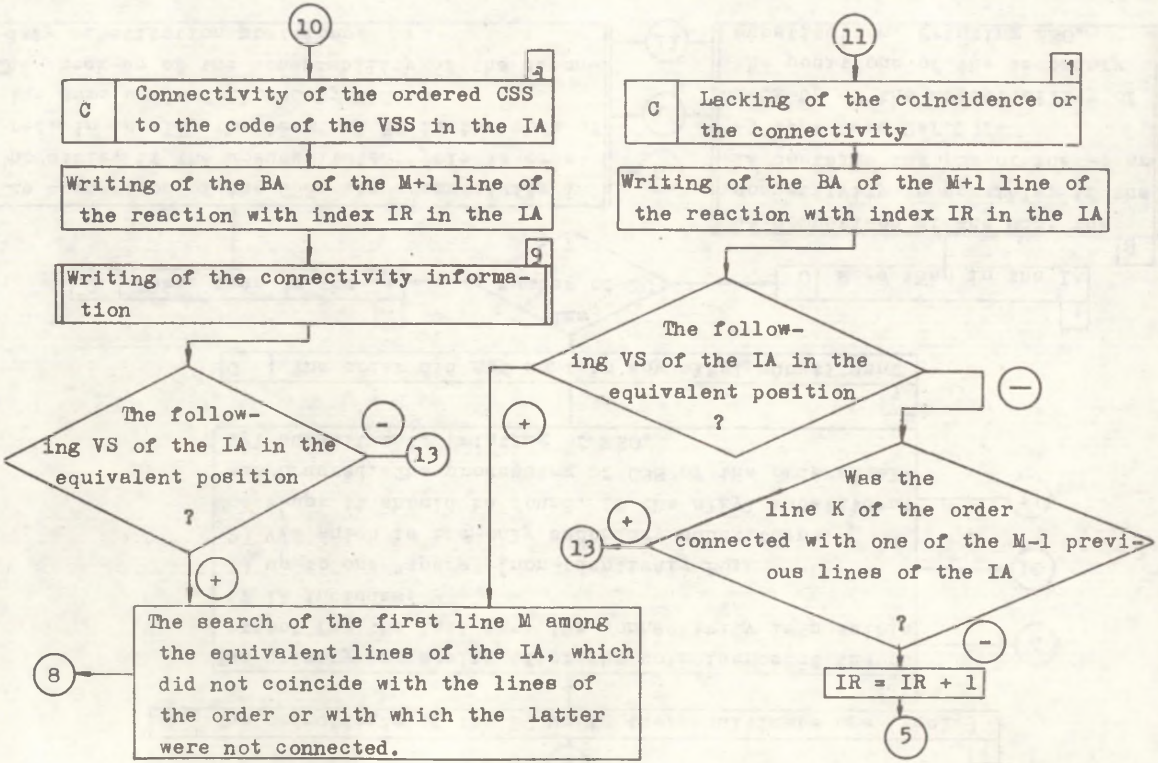
PRINCIPLED FLOW CHART OF REACTION SEARCH PROGRAM

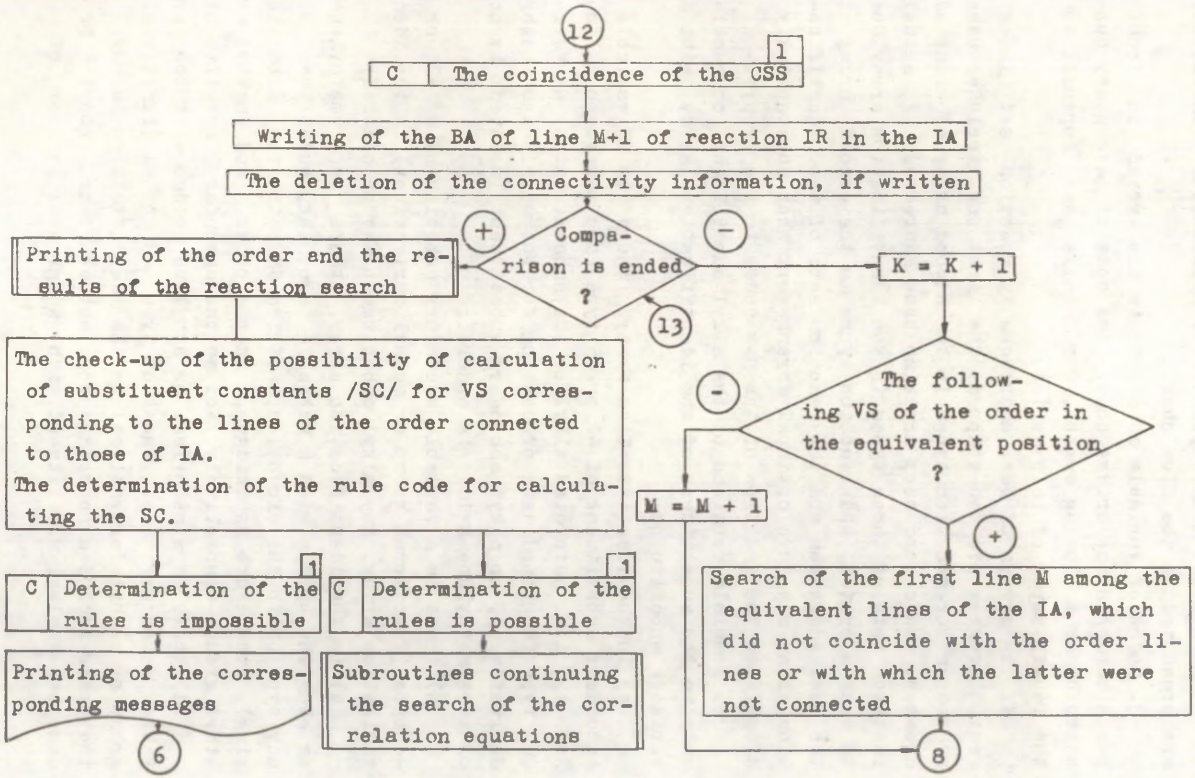



3
"See message to the previous job"
2
Move-in of the continuation constant /KCC/
4
Analysis of the CVS "Inversion" of the CVS if KI = 1
1'
C
The same type of the reaction is ordered with new VS or in another solvent
≠0
≠4
KCC = ?
=4
=0
1
STOP
4
Determination of the base address /BA/ of the reaction type RTI in the identification array /IA/
1
C
Exits if there are errors when moving in CVS
5
Determination of the BA for the next actual reaction with the index IR of the RTI type
"Error in the order: to long line [I]" or other messages
Print of the order and the message: "There is no reaction registered"
=0
BA = ?
>0
7
6
No-operation move-in of the other data of the order
Move-in of the KCC
KCC = ?
=0
STOP
=4
=3
"See message to the previous job"
1
C
The same reaction is ordered in different conditions
=1(2)
1
4


7
K = 1, M = 1
The outset of the comparison of the order line K with the line M of the IR reaction in the IA
8
9
Comparison of bridge codes /BC/
1
C
Full coincidence of the ordered BC with those of IA
=0
The number of IA?
> 0
7
The comparison of the codes of secondary substituents /CSS/.
The check-up of the type correspondence of CSS in case of variable secondary substituent /VSS/ in IA.
Printing of the messages about the errors in the order /MEO/
6
10
11
12
6
The comparison of CSS depending on the type of the terminal bridge (see clause 5.1 in Ref.1).
The check-up of the acceptability of the number and the position of the secondary substituents if the terminal bridge is ethylene fragment, COPS or CMPS.
The check-up of the type correspondence of CSS in case of variable secondary substituent /VSS/ in IA.
The printing of MEO or messages about the failures by program activities.


9
1
C
The coincidence of the BC up to the penultimate one (incl.)
5
The primary processing after the coincidence of the BC except for the last one: the connectivity is possible if IA includes:
1) up to one "spare" (non-identical) BC;
2) VVS which is the only secondary substituent.
Check-up: it should be found, if the alkyl substituent was ordered. The processing of CSS of the ordered alkyl substituent. Printing of MEO.
6
10
11
1
C
The order did not contain any alkyl substituent
The number of BC ?
1
C
Fewer than in the IA
1
C
More than in the IA
The comparison of the CSS: the connectivity is possible, if the unsubstituted cycle is ordered; in the IA, the terminal BC is the code of the same cycle followed by VSS.
The check-up of the acceptability of the secondary substitution positions.
6
10
11
8
The comparison of the CSS: the connectivity is possible, if the IA contains the VSS of the -4 or -5 type (see Ref.1).
Check-up of the acceptability of the positions of the secondary substitution. Printing MEO.


10
11
C
Connectivity of the ordered CSS to the code of the VSS in the IA
4
C
Lacking of the coincidence or the connectivity
1
Writing of the BA of the M+1 line of the reaction with index IR in the IA
Writing of the BA of the M+1 line of the reaction with index IR in the IA
Writing of the connectivity information
9
The following VS of the IA in the equivalent position ?
The following VS of the IA in the equivalent position ?
-
+
13
Was the line K of the order connected with one of the M-1 previous lines of the IA ?
IR = IR + 1
5
The search of the first line M among the equivalent lines of the IA, which did not coincide with the lines of the order or with which the latter were not connected.
8


12
C
1
The coincidence of the CSS
Writing of the BA of line M+1 of reaction IR in the IA
The deletion of the connectivity information, if written
+
Comparison is ended ?
−
13
Printing of the order and the results of the reaction search
K = K + 1
The check-up of the possibility of calculation of substituent constants /SC/ for VS corresponding to the lines of the order connected to those of IA.
The determination of the rule code for calculating the SC.
-
The following VS of the order in the equivalent position ?
M = M + 1
+
C
1
Determination of the rules is impossible
C
1
Determination of the rules is possible
Search of the first line M among the equivalent lines of the IA, which did not coincide with the order lines or with which the latter were not connected
Printing of the corresponding messages
Subroutines continuing the search of the correlation equations
6
8

tual messages are always printed in Russian, the translations are presented in the flow chart.

3. Codes of variable substituents are moved in from punch cards in one bridge code, the code of secondary substituent or a closing symbol. For details see Appendix to the fourth paper of this series.

4. The arrays of base addresses in reaction set index search program are two-stepped: the first one includes base addresses for reaction types in the second array of base addresses, the second step contains base addresses of actual reaction sets of these types in the identification array. Due to such a system, the reaction types in the second array of the base addresses and the reaction sets of the identification array may have optional arrangement what substantially simplifies the addition of the new codes to the arrays.

5. Possible versions of the alkyl substituent connectivity to the substituent of the identification array with a variable substituent:

a) in the identification array, there is a variable secondary substituent of -2 or -5 type (see paragraph 4 in Ref. 1), i.e. saturated alkyl or the substituent or a "mixed" type (combined data processing for the alkyls and methyl derivatives), an alkyl secondary substituent isolated by one or more methylene bridge is ordered;

b) there is a variable secondary substituent of -3 or -4 type (functional group or methyl derivatives) in the identification array, any alkyl substituent may be ordered;

c) in the identification array, there is a methylene or ethylene bridge with a variable secondary substituent of any type (with the exception, of the VSS in the aromatic ring), there are no bridges, in the order, and methyl or ethyl group, respectively, act as the secondary substituent;

d) there is a methylene or ethylene bridge with the variable secondary substituent of type -3 or -4 (functional group or methyl derivatives) in the identification array, the order includes no bridge code but ethyl or propyl (or some other alkyl substituent with a greater number of

chains), respectively, are the secondary substituents.

6. The proof of the feasibility of the ordered number and positions of secondary substituents comprises the following processes:

a) if the terminal bridge is methylene, ethylene or some other aliphatic fragment (a bridge of the OB group, see paragraph 5.1. in Ref. 1), the order may contain one secondary substituent, only;

b) if the terminal bridge is a cycle with one position of secondary substitution (a bridge of the GOPS group[1]) - the same. Moreover, if the code of the secondary substituent is ordered, indicating the position, its correctness is checked;

c) if the terminal bridge is a cycle with more than one acceptable position of secondary substitution (a bridge of the GMPS group[1]), there are two possibilities:

- if the identification array contains a variable secondary substituent, only, the acceptability of the positions of the ordered substituents is checked;

- if the identification array contains, besides the variable substituent, also some other secondary substituents, their coincidence with the order is checked. In the case of their coincidence, the codes of non-identical secondary substituents of the order are given via the common field to the program for writing of connectivity information.

7. See 6a).

8. The connectivity of the ordered substituent to a substituent of the identification array with variable secondary substituent of the -4 or -5 type (methyl derivative or "mixed" type substituent) can be observed with the following versions of the order (only the part following the codes which fully coincide with the codes of the corresponding line of the identification array has been presented):

a) the terminal bridge is methylene, the secondary substituents are alkyls and/or functional groups (and substituents equated with them);

b) the terminal bridge is ethylene, the secondary

groups are alkyls and/or functional groups (and substituents equated with them), substitution positions are indicated;

c) two methylene bridges, the secondary substituents are presented in 8a).

9. The connectivity information includes the following constants: the code of the terminal bridge, the type index of the variable secondary substituent, the codes of the ordered secondary substituents (with/without indication of the position of the secondary substitution) connected to the variable secondary substituents of the identification array, as well as the array with the arrangement of the coincidence and connectivity of substituents /AAS/. If line K of the order coincides with "line" M of the identification array then the item of the AAS array with index K' is equalled to M, if there is no coincidence, but the connectivity can be observed, this item is equated to -M.

Thus, the positive result of the action of the described segments of the program package lies in the establishing of the coincidence (connectivity) of the ordered reaction codes and the codes of variable substituents with the corresponding items of the identification array as well as in the existing of rules for the further activities according to the search data. Output data given to the other segments of the program package include the index of the reaction set, the connectivity information and the rule code for calculation of substituent constants.

The negative result is obtained if either the ordered reaction code does not coincide with any of those belonging to the reaction codes' array; at least one ordered code of the variable substituent does not coincide with the codes of the identification array; it is not possible to calculate the substituent constants for the connected structural fragments; or if there are some errors in the user's order. In every definite case, the corresponding message about the character of the error, the failure or the impossibility to solve the order is printed. After that the program guarantees the no-operation input of the other data of the

unsolved order and the passing over to a new order if there is any.

References.

1. T.J. Jüriado and V.A. Palm, Organic Reactivity 21, 255(1984).

Organic Reactivity
Vol.21. 4(76) 1984

PROGRAM PACKAGE FOR COMPUTER STORAGE AND AUTOMATIC SEARCH OF CORRELATION EQUATIONS AND FOR CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS.
3. ALGORITHM FOR SEARCH OF SOLVENT AND TEMPERATURE.

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The algorithm of program segments for search of the ordered solvent and temperature has been presented. The solvent search includes the comparison of the indexes of the ordered solvents or the summary codes formed from the indexes and the concentration indicators of the solvent compounds with the corresponding items of the program information arrays. The search of the temperature is carried out if the search of the solvent ends with a positive result. This search includes a direct comparison of the ordered values with those inserted into the information arrays of the program.

In the previous paper of this series, the algorithm for the search of the reaction set index from the identification arrays on the basis of reaction and substituent codes has been described. The result of this search is the assignment of the known values to the index of the reaction set /IRS/, to the rule code for calculation of substituent constants /RCCC/ and to the constants indicating the type of connectivity of the ordered substituents to the substituents with

a variable secondary substituent /VSS/ of the identification array /IA/.

Below, the algorithm of the using of the IRS value in the other segments of the program up to the completion of the reaction set search is described.

1. The Search of the Solvents.

The initial data of the program segments which guarantee the search of the reaction set in the ordered solvent are the index of the reaction set and the user's solvent order /SO/ (moved in from punch cards). The SO consists of the indexes of the compounds /IC, from one to three/, the concentrations of the second and third compounds /CC/, if there are any, and the indexes of their concentration dimension /ICD/. For the ICD, the following values are accepted:

0 - mole per cent,
1 - volume per cent,
2 - weight per cent,
3 - concentration in moles.

In the array of the solvent codes, there could be the additional value ICD = 4 denoting the unknown (volume or weight) percentage.

The program segment executes the search of the solvent and ending their activities with the positive result (i.e. in the arrays, there are the data for calculation of the ordered constant in the ordered solvent) assigns the values to the constants and array items named together the information about the found solvent(s) /IAFS/. In case of a negative result, the program puts out the information concerning these solvents the data about which is contained in the program arrays. The IAFS consists of three constants - the index of the reaction set in the ordered solvent, the indicator of the coincidence type of the solvent and the index of the found solvent - and three arrays including the values of the compound concentrations and the indexes of the corresponding reaction sets for mixed solvents.

The search of the solvent includes the comparison of the solvent user's order (for pure (unicomponent) solvents) or

the summary code formed from the user's order of the binary or ternary solvents with the items of the arrays of solvent codes /ASC/.

The ASC are divided into the array of base addresses, the code array of binary solvents with two auxiliary arrays, the code array of ternary solvents with two auxiliary arrays and the array of solvent indexes.

The item indexes of the array of base addresses are, in the substance, the indexes of reaction set /IRS/, any item of the array indicates the base address of the reaction set with the IRS index in the array of the solvent indexes /ASI/. The items of the ASI array /IASI/, in their turn, could be:

- the direct codes (indexes) of the pure solvents ($0 < IASI < 1000$)

which are taken from the "Tables"[2] and presented in Table 1;

- the indicators of correlation equations with pure solvents as a variable factor ($IASI < 0$),

- the indicators of the binary ($1000 > IASI > 3000$) or ternary solvents ($IASI < 3000$), /IBS and ITS, respectively/.

The difference [IBS - 1000] corresponds to the item index of the code array of binary solvents, [ITS - 3000]- that of the ternary solvents. The summary codes of such mixed solvents, only, in which the parameters of correlation equations are known, are inserted into the arrays of the codes of binary and ternary solvents.

The summary code of a binary solvent in the code array of binary solvents /SCBSA/ is expressed as

$$SCBSA = ISP + CS2 \cdot 10^5 + ICD \cdot 10^7,$$

where ISP, CS2 and ICD are the indexes of the solvent pair in the binary solvent, the concentration of the second compound and the index of the concentration dimension. There are two auxiliary arrays for decoding of the IPS whose items with indexes K are respectively the summary code of the solvent pair /SCSP/ and ISP. The SCSP code is formed as

$$SCSP = IS1 \cdot 10^3 + IS2,$$

where IS1 and IS2 are the indexes (from Table 1) of the first

and second compound of the binary solvent.

The arrays of the ternary solvents /ATS/ are formed analogically. The summary code of the ternary solvent /SCTSA/ is presented as two items of ATS array following one after another

$$ATS(K) = ICD3 \cdot 10^4 + ICD2 \cdot 10^3 + IST$$
$$ATS(K+1) = CS2 \cdot 10^6 + CS3 \cdot IO^2 ,$$

where K is the odd index of the ATS array; IST, CS2, CS3, ICD2 and ICD3 are the index of the solvent triplet in the ternary solvent, the concentrations of the second and third compound, and their dimension indexes, respectively. The items of the auxiliary arrays form the compound code of the solvent triplet /CCST/ and IST, respectively. The CCST code is formed as

$$CCST = IS1 \cdot 10^6 + IS2 \cdot 10^3 + 1S3,$$

where IS1, IS2 and IS3 are the indexes of the three compounds.

All subarrays of solvent codes could be supplemented with new data without any remarkable difficulties.

The solvent order is put in (from punch cards, in our version) as follows:

a) for pure solvents - one description (punch card) with the solvent index;

b) for binary solvents - one description (card) with the index of the first compound, the second one with the index, concentration and the concentration dimension index of the second compound;

c) for ternary solvents - the same and the third description (card) with the index, concentration and the concentration dimension index of the third compound.

The compounds of binary and ternary solvents are to be ordered in the order of the increase of the solvent indexes. For further details, see Appendix to the next paper of this series.

Below, the activities of the program when ordering the solvents of various types are presented.

1.1. The Pure Solvent is Ordered.

The base address for the array of solvent indexes /ASI/ of the reaction set with the IRS index is found from the ar-

ray of the base addresses. At the first stage of the comparison, the items of the ASI array IASI < 1000 (i.e. pure solvents and the correlation equations with pure solvent as a variable factor), only, are considered. The coincidence of the ordered solvent index with IASI is found. Simultaneously, the indexes of the other pure solvents are written in the auxiliary arrays. If there are any correlation equations with pure solvents as a variable factor, their codes and reaction set indexes are written, too. If the coincidence of the ordered index with the IASI is found, the index of the reaction set in the ordered solvent /IRSS/ (equated to the IRS index) and the indicator of the solvent's coincidence type (equated to zero) are given via the common field to the other program segments.

If no coincidence but the correlation equation with the pure solvent (or some type of the pure solvent) as a variable factor is found, the IRSS is equated to the index of that reaction set and the indicator of the coincidence type of the solvent - to the code of the correlation equation. The index of the found solvent is equated to the index of the ordered solvent. In both cases, the operation of the program continues with the search of temperature.

In case of negative result (i.e. if there is no possibility of calculating the ordered constants neither according to the equation for the pure solvent nor by means of the correlation equation with the pure solvent as a variable factor), then is printed the message indicating all the pure solvents in which the data for the ordered reaction can be calculated. During the following cycle of comparison are found the binary solvents containing the ordered solvent. The double indexes of those binary solvents are printed as [IS1] / [IS2]. For such and similar cases, the control blocks of the program are meant: if the constants for the same reaction in various solvents are ordered, it is checked up, whether the list of solvents, mentioned above, has already been printed or not. In the last-mentioned case, the message: "See message to the previous job" (in Russian) is printed, only.

1.2. The Binary Solvent is Ordered.

The search begins with the formation of the ordered solvents pair index (analogically with the formation of the SCSP codes in the information array) and of the binary solvent summary code /SCBS/ whose structure is identical with that of the summary code in the codes' array of binary solvents /SCBSA/. When the base address has been obtained, follows the first cycle of comparison, in the course of which the binary systems of the array of solvent codes (1000 < IASI < 3000) are taken into consideration. First of all, the coincidence of the SCBS with the SCBSA is searched.

At the same time, the following actions are accomplished :

a) the correlation equation with the mole percentage of the ordered solvents pair as a variable factor is searched. If there is any, its index is written;

b) the concentration of the second compound and the indexes of the corresponding reaction sets for the binary system of the array of the solvent codes /ASC/ which coincide with the order in the solvent pair but differ in the compounds' concentration are written into the auxiliary arrays;

c) the summary codes of the solvent pair /SCSP/ for the solvents having a common compound with the ordered solvents are written into another auxiliary array.

If the coincidence of the SCBS with the SCBSA is found, the actions mentioned in statements a) - c) are discontinued, the index of the reaction set in the ordered solvent /IRSS/ is equated to the value of the index of the corresponding reaction set /IRS/, the indicator of the coincidence type to zero and the index of found solvent - to the concentration value of the second compound multiplied by a hundred.

If there is no coincidence, the presence of the correlation equation with the mole percentage as a variable factor is checked up. If there is such an equation, the IRSS is equated to the index of the corresponding set and the indicator of the coincidence type to a unity.

The third version of the positive result presumes the presence of binary systems coinciding with the order in the solvents' pair and the dimension indicator of the concentration but differing in the concentration. The versions with their corresponding indexes of reaction sets included into the code arrays of the solvents are written into the information arrays of the found solvents /IAFS/ while the reaction set index's value in the ordered solvent /IRSS/ equals 0 (in case of various concentrations) or -1 (in case of only one concentration level, differing from the concentration order). The indicator of the coincidence type is equated to the number of the found version and to zero, respectively. If the dimension indicator of the concentration in the solvent array differs from that of the order, too, enabling to obtain the positive results if the order is repeated, the corresponding messages are printed.

In all the above-mentioned cases follows the return to the main routine in order to find the temperature.

If the positive result cannot be achieved and the lists of the systems present in the array of solvent codes /ACS/ were not printed in previous jobs, there are two possible continuations:

a) there are data for calculation of the constants for binary systems having a common compound with the ordered one. Then the existence of the data for the compounds of the ordered solvents as pure solvents as well as the presence of the correlation equations with the pure solvents as a variable factor are found. All mentioned data are printed.

b) if there was no coincidence concerning the solvent, the lists of those solvents for which there are data of the ordered reaction in the information arrays are printed.

1.3. A Ternary Solvent is Ordered.

Generally, the operations of the program are similar with those described in paragraph 1.2. keeping, of course, in mind, that in the first cycle of the comparison the ternary systems of the array of solvents codes (IASI > 3000) are considered. At first, the coincidence of the solvent triplet index

and of the corresponding part of the ternary solvent code formed from the solvent order is searched. Simultaneously the concentrations, non-identical with the order, of the same solvent triplet as well as the data about correlation equations with the mole percentage as a variable factor, are written into the auxiliary arrays. The data on the binary and ternary systems which have two common compounds with the ordered solvents are fixed into the auxiliary arrays, too.

Positive results are similar with those described for binary solvents. In the case of negative results the list of binary and ternary systems which have two common compounds with the ordered solvent is printed, if it has not been done in the previous jobs.

All cases with negative results both for pure and binary or ternary solvents are followed by the no-operation move-in of the temperature order and operational move-in of the continuation constants /KCC, see in Ref. 1/.

When carring out the program of the solvent search various messages about failures and errors may occur, after which depending on the character of the disorder the job is either stopped or continued, passing on to the next activities as in case of negative results.

2. The Search of the Temperature.

Every order may contain up to three temperatures for one reaction. The temperatures are moved in one by one (from punch cards), for details see the Appendix to the next paper of this series.

Temperature data are inserted into the following arrays:

- the array of base addresses. The elements of its items are, in their content, the indexes of the reaction sets in the ordered solvents /IRSS/, the items themselves indicate the base addresses of the reaction sets with the IRSS indexes in the temperature array /TA/;

- the temperature array /TA/, whose may have the following values:

a) T = -500. - the correlation of data, for which the

temperature is not indicated;

b) T > 1000. - the variable temperature code, i.e. for this reaction set the temperature is one of the variable factors in the correlation equation. Difference K = T - 1000. equals the index of the array of temperature intervals /ATI/;

c) T = -1000. - vacant code (the closing symbol of the temperature list for a current reaction);

d) all other T-values are equal to actual temperatures. The indexes of the items of the MT array are, in their content, the indexes (sequence numbers) of correlation equations.

The temperature search is carried out after positive result of the solvent search, only. There are three different versions of the temperature search depending on the results of the solvent search:

a) a full coincidence of the ordered solvent is established or the correlation equation with the solvent as the variable factor is found. If the exact temperature value is not obtained, the indexes of correlation equations for the ordered reaction are defined (the rate or equilibrium constants are calculated) at all possible temperatures. If the ordered temperature coincides with that of the temperature array or the program uses the correlation equation with a variable temperature, the calculation of constants at the ordered temperature is realized;

b) one (for binary solvents) or more systems (for ternary solvents) with non-identical concentration are found. At first, the coincidence of the temperature is checked. If there is no coincidence, the data at the nearest temperature when equated with the ordered temperature are taken for calculations;

c) some binary systems with non-identical concentrations are found. The temperatures are taken into account, only. If they are absent, the message "There are no data to carry out correlation at T^{o}= [T]" (in Russian) is printed.

When the search of the temperature value is ended, the following data are given over for further operations of the program: the ordered temperature value, the index of the cor-

Table 1

Codes of Pure Solvents

Code	Solvent Formula	Code	Solvent Formula
1.	H_2O	23.	$C_6H_5CH_2CH_2OH$
2.	D_2O	24.	$C_6H_5(CH_2)_3OH$
3.	CH_3OH	25.	$CH_2{=}CHCH_2OH$
4.	C_2H_5OH	26.	$CH{\equiv}CCH_2OH$
5.	C_3H_7OH	27.	$HOCH_2CH_2OH$
6.	C_4H_9OH	28.	$CH_3OCH_2CH_2OH$
7.	$C_5H_{11}OH$	29.	$C_2H_5OCH_2CH_2OH$
8.	$C_6H_{13}OH$	30.	$C_4H_9OCH_2CH_2OH$
9.	$C_7H_{15}OH$	31.	$(HOCH_2CH_2)_2O$
10.	$C_8H_{17}OH$	32.	$CH_3CH(OH)CH_2OH$
11.	$ClCH_2CH_2OH$	33.	$CH_2(OH)CH(OH)CH_2OH$
12.	$(CH_3)_2CHOH$	34.	CF_3CH_2OH
13.	$(CH_3)_2CHCH_2OH$	35.	$(CF_3)_2CHOH$
14.	$(CH_3)_2CHCH_2CH_2OH$	36.	H_2O_2
15.	$(CH_3)_3COH$	265.	$C_{12}H_{25}OH$
16.	$(CH_3)_2(C_2H_5)COH$	266.	$(CH_3)_2CH(CH_2)_5OH$
17.	$CH_3(C_2H_5)CHOH$	267.	$CH_3CH_2CH_2CH(OH)CH_3$
18.	$(C_2H_5)_2CHOH$	305.	$HO(CH_2CH_2O)_2CH_2CH_2OH$
19.	$c\text{-}C_5H_9OH$	325.	$C_{10}H_{21}OH$
20.	$c\text{-}C_6H_{11}OH$	326.	$C_6H_{13}CH(CH_3)OH$
21.	$C_6H_5CH_2OH$	327.	$NH_2CH_2CH_2OH$
22.	$C_6H_5CH(CH_3)OH$	328.	$C_2H_5(OCH_2CH_2)_2OH$
37.	C_6H_5OH	273.	$CH_3COCH_2CH_2Ph$

Table 1 continued

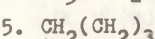
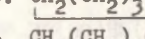
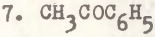
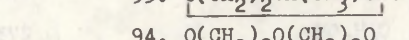
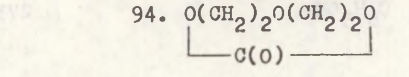
Code	Solvent	Formula	Code	Solvent	Formula
38.		$2\text{-}CH_3\text{-}C_6H_4OH$	51.		CH_3CHO
39.		$3\text{-}CH_3\text{-}C_6H_4OH$	52.		C_6H_5CHO
304.		$2\text{-OMe-4-}(CH_2CH{=}CH_2)\text{-}C_6H_3OH$	53.		$CH_2{=}CHCHO$
329.		$3\text{-}CH_3\text{-}C_6H_{10}OH$	54.		
330.		$4\text{-}CH_3\text{-}C_6H_4OH$	303.		CH_2O
331.		$4\text{-Cl-}C_6H_4OH$	55.		$HCOOH$
40.		$(CH_3)_2CO$	56.		CH_3COOH
41.		$CH_3COC_2H_5$	57.		C_2H_5COOH
42.		$(C_2H_5)_2CO$	58.		C_3H_7COOH
43.		$CH_3COC_4H_9$	59.		C_4H_9COOH
44.		$CH_3COCH_2CH(CH_3)_2$	60.		$C_5H_{11}COOH$
45.			61.		$C_7H_{15}COOH$
46.			62.		$(CH_3)_2CHCOOH$
47.		$CH_3COC_6H_5$	63.		CF_3COOH
48.		$CH_3COCH_2COCH_3$	64.		HNO_3
49.			65.		$HClO_4$
50.		$(C_6H_5)_2CO$	66.		H_2SO_4
268.		$CH_3COC_3H_7$	67.		H_3PO_4
269.		$C_3H_7COC_3H_7$	68.		HCl
270.		$C_2H_5COC_4H_9$	274.		$ClCH_2COOH$
271.		$CH_3COCH_2CH_2COCH_3$	306.		CH_3SO_3H
272.		CH_3COCH_2Ph	313.		HF
69.		$(CH_3CO)_2O$	92.		$C_6H_5CH{=}CHCOOC_2H_5$
70.		$(C_2H_5CO)_2O$	93.		
71.		$HCOOCH_3$	94.		
72.		$HCOOC_2H_5$			

Table 1 continued

Code	Solvent Formula	Code	Solvent Formula
73.	CH_3COOCH_3	95.	$CH_3COOCH_2CH(CH_3)_2$
74.	$CH_3COOC_2H_5$	96.	$CH_3COCH_2COOC_2H_5$
75.	$CH_3COOC_4H_9$	275.	$EtOOCCH_2COOH$
76.	$CCl_3COOC_2H_5$	276.	trans-EtOOCCH= =CHCOOEt
77.	$CH_2ClCOOC_2H_5$		
78.	$CNCH_2COOC_2H_5$	277.	$MeOOCCH_2CH_2COOMe$
79.	$C_2H_5COOC_2H_5$	278.	$OCH_2CH_2CH_2CO$
80.	$C_6H_5COOCH_3$	279.	OCH_2CH_2OOC
81.	$C_6H_5COOC_2H_5$	280.	$OCH_2CH(CH_3)OOC$
82.	$(C_2H_5)_2CO_3$	281.	$OCH_2CH_2CH_2OOC$
83.	$(COOC_2H_5)_2$	307.	$1,2-(COOEt)_2-C_6H_4$
84.	$CH_2(COOC_2H_5)_2$	332.	$1,4-[OOC(4-OHex-..-C_6H_4)]_2-C_6H_4$
85.	$C_2H_5OOCCH=CHCOOC_2H_5$		
86.	$(C_2H_5)_3PO_4$	97.	$HCONH_2$
87.	$1,2-(C_4H_9COO)_2-C_6H_4$	98.	$HCONHCH_3$
88.	$(C_4H_9)_3PO_4$	99.	$CH_3CONHCH_3$
89.	$(C_6H_5)_3PO_4$	100.	$C_2H_5CONHCH_3$
90.	$(3-CH_3-C_6H_4)_3PO_4$	101.	$C_2H_5CONHC_2H_5$
91.	$(CH_3)_2SO_4$	102.	$HCON(CH_3)_2$
103.	$CH_3CON(CH_3)_2$	119.	$(C_2H_5)_2O$
104.	$CH_3CONHC_4H_9$	120.	$(C_3H_7)_2O$
105.	CH_3CONH_2	121.	$(C_4H_9)_2O$
106.	$PO[N(CH_3)_2]_3$	122.	$[(CH_3)_2CH]_2O$
107.	HCN	123.	$(C_5H_{11})_2O$
108.	CH_3CN	124.	$[(CH_3)_2CHCH_2CH_2]_2O$

Table 1 continued

Code	Solvent Formula	Code	Solvent Formula
109.	C_2H_5CN	125.	$(CH_2{=}CHCH_2)_2O$
110.	C_3H_7CN	126.	OCH_2CHCH_2Cl
111.	C_4H_9CN	127.	$(ClCH_2CH_2)_2O$
112.	$C_5H_{11}CN$	128.	$C_6H_5OCH_3$
113.	$NCCH_2CH_2CH_2CN$	129.	$C_6H_5OC_2H_5$
114.	$NC(CH_2)_8CN$	130.	$(C_6H_5)_2O$
115.	$NC(CH_2)_{10}CN$	131.	$(C_6H_5CH_2)_2O$
116.	C_6H_5CN	132.	$(CH_3O)_2CH_2$
117.	$C_6H_5CH_2CN$	133.	$(CH_3OCH_2)_2$
118.	$CH_2{=}CHCN$	134.	$(C_2H_5OCH_2)_2$
282.	$(CH_3)_2CHCN$	135.	$(C_2H_5OCH_2CH_2)_2O$
283.	$(CH_3)_2CHCH_2CN$	136.	$HC{=}CH{-}CH{=}CH{-}C$
284.	$(CH_3)_3CCN$	137.	$CH_2(CH_2)_3O$
285.	$C_{11}H_{23}CN$	138.	$C_2H_5OCH(CH_3)_2$
286.	$C_{13}H_{27}CN$	139.	$CH_2CH_2O(CH_2)_2O$
287.	$PhCH_2CN$	140.	$(CH_3OCH_2CH_2)_2O$
288.	trans-$NCCH{=}CHCN$	289.	$C_2H_5OC_3H_7$
333.	$NC(CH_2)_4CN$	290.	$C_2H_5OCH_2CH_2CH(CH_3)_2$
291.	$(CH_3)_3COCH_2CH_2OH$	157.	$C_6H_5N(CH_3)_2$
292.	2-Me-$C_6H_4CH_3$	158.	$C_6H_5N(C_2H_5)_2$
293.	3-Me-$C_6H_4CH_3$	159.	C_5H_5N
294.	4-Me-$C_6H_4CH_3$	160.	C_9H_7N
295.	$CH_3(OCH_2CH_2)_3OCH_3$	161.	$2\text{-}CH_3C_5H_4N$
296.	$CH_3(OCH_2CH_2)_4OCH_3$	162.	$2,6\text{-}(CH_3)_2C_5H_3N$
308.	$CH_2{=}CHOBu$	163.	CH_3NO_2

Table 1 continued

Code	Solvent Formula	Code	Solvent Formula
141.	$C_4H_9NH_2$	164.	$C_2H_5NO_2$
142.	$C_6H_5CH_2NH_2$	165.	$C_3H_7NO_2$
143.	$C_6H_5NH_2$	166.	$C_6H_5NO_2$
144.	NH_3	297.	$C_6H_{13}NO_2$
145.	$2\text{-}CH_3C_6H_4NH_2$	298.	$2\text{-}NO_2\text{-}C_6H_4CH_3$
146.	H_2NNH_2	299.	$3\text{-}NO_2\text{-}C_6H_4CH_3$
147.	$(CH_3)_3CNH_2$	300.	$4\text{-}NO_2\text{-}C_6H_4CH_3$
148.	$C_3H_7NH_2$	301.	$4\text{-}NO_2\text{-}C_6H_4OCH_3$
334.	$C_{10}H_{21}NH_2$	314.	$(CH_3)_2CHNO_2$
149.	$C_5H_{11}N$	167.	SO_2
150.	$CH{=}CH{-}CH{=}CH{-}NH$	168.	$(CH_3)_2SO$
151.	$HN{=}C[N(CH_3)_2]_2$	169.	$CH_2(CH_2)_2CH_2SO_2$
152.	$C_6H_5NHCH_3$	170.	$CH(CH_3)(CH_2)_2CH(CH_3)SO_2$
153.	$C_6H_5NHC_2H_5$	171.	$(C_2H_5)_2S$
154.	$(C_2H_5)_3N$	172.	CS_2
155.	$(C_3H_7)_3N$	173.	$CH{=}CH{-}CH{=}CH{-}S$
156.	$(C_4H_9)_3N$	174.	C_2H_5SH
308.	$CH(CH_3)CH_2CH(CH_3)CH_2SO_2$	194.	$C_6H_5C{\equiv}CH$
315.	SO_3	195.	$1,2\text{-}(CH_3)_2\text{-}C_6H_4$
316.	$C_6H_5SO_2Cl$	196.	$1,3\text{-}(CH_3)_2\text{-}C_6H_4$
175.	$CH_3CH(CH_3)C_2H_5$	197.	$1,4\text{-}(CH_3)_2\text{-}C_6H_4$
176.	$CH_3(CH_2)_3CH_3$	198.	$1\text{-}CH_3\text{-}4\text{-}CH(CH_3)_2\text{-}C_6H_4$
177.	$CH_3(CH_2)_4CH_3$	199.	$1,3,5\text{-}(CH_3)_3\text{-}C_6H_3$
178.	$CH(CH_3)(C_2H_5)_2$	200.	$(CH_3)_6C_6$
179.	$CH_3(CH_2)_5CH_3$	201.	$CH_2(C_6H_5)_2$
180.	$(CH_3)_3CCH_2CH(CH_3)_2$	202.	$C_6H_5C_6H_5$

Table 1 continued

Code	Solvent Formula	Code	Solvent Formula
181.	$CH_3(CH_2)_6CH_3$	203.	$C_{10}H_8$
182.	$CH_3(CH_2)_8CH_3$	204.	$1\text{-}CH_3\text{-}C_{10}H_7$
183.	$c\text{-}C_5H_{10}$	205.	$C_{10}H_{12}$
184.	$c\text{-}C_6H_{12}$	309.	$1,2,4\text{-}(CH_3)_3\text{-}C_6H_3$
185.	$CH_3C_6H_{11}$	337.	$C_4H_9CH{=}CH_2$
186.	$C_{10}H_{18}$	206.	CH_2Cl_2
335.	$CH_3(CH_2)_{12}CH_3$	207.	$CHCl_3$
336.	$CH_3(CH_2)_{14}CH_3$	208.	CCl_4
187.	$CH_2{=}CHC(CH_3){=}CH_2$	209.	$CHCl_2CH_3$
188.	C_6H_{10}	210.	$ClCH_2CH_2Cl$
189.	C_6H_6	211.	CH_3CCl_3
190.	$C_6H_5CH_3$	212.	$CHCl_2CH_2Cl$
191.	$C_6H_5C_2H_5$	213.	$CHCl_2CHCl_2$
192.	$C_6H_5CH(CH_3)_2$	214.	CCl_3CHCl_2
193.	$C_6H_5CH{=}CH_2$	215.	$cis\text{-}CHCl{=}CHCl$
216.	$trans\text{-}CHCl{=}CHCl$	319.	$CFCl_3$
217.	$CHCl{=}CCl_2$	320.	$CFCl_2CF_2Cl$
218.	$CCl_2{=}CCl_2$	321.	$1,2,4\text{-}Cl_3\text{-}C_6H_3$
219.	C_3H_7Cl	338.	OCH_2CHCH_2Cl
220.	$CH_2{=}CHCH_2Cl$	238.	Br_2
221.	C_4H_9Cl	239.	CH_2Br_2
222.	$(CH_3)_2CHCH_2Cl$	240.	$CHBr_3$
223.	$(CH_3)_3CCl$	241.	C_2H_5Br
224.	$Cl(CH_2)_4Cl$	242.	$BrCH_2CH_2Br$
225.	$C_6H_{13}Cl$	243.	C_3H_7Br
226.	$c\text{-}C_6H_{11}Cl$	244.	$(CH_3)_2CHBr$

Table 1 continued

Code	Solvent Formula	Code	Solvent Formula
227.	C_6H_5Cl	245.	$CH_2=CHCH_2Br$
228.	$1\text{-}CH_3\text{-}2\text{-}Cl\text{-}C_6H_4$	246.	C_4H_9Br
229.	$1\text{-}CH_3\text{-}3\text{-}Cl\text{-}C_6H_4$	247.	$(CH_3)_3CBr$
230.	$1\text{-}CH_3\text{-}4\text{-}Cl\text{-}C_6H_4$	248.	$C_{12}H_{25}Br$
231.	$1,2\text{-}Cl_2\text{-}C_6H_4$	249.	$c\text{-}C_6H_{11}Br$
232.	$1,3\text{-}Cl_2\text{-}C_6H_4$	250.	C_6H_5Br
233.	$1,4\text{-}Cl_2\text{-}C_6H_4$	251.	$1\text{-}Br\text{-}C_{10}H_7$
234.	$1\text{-}Cl\text{-}2\text{-}NO_2\text{-}C_6H_4$	318.	CH_3Br
235.	$1\text{-}Cl\text{-}4\text{-}NO_2\text{-}C_6H_4$	252.	CH_3J
236.	$C_6H_5CH_2Cl$	253.	CH_2J_2
237.	$1\text{-}Cl\text{-}C_{10}H_7$	254.	C_2H_5J
310.	$CFCl_2CFCl_2$	255.	C_3H_7J
317.	CH_3Cl	256.	$(CH_3)_2CHJ$
257.	C_4H_9J	263.	$GeCl_4$
258.	C_6H_5J	264.	$SbCl_5$
259.	C_5F_{12}	311.	$CH_3CH=CHCOCl$
260.	C_7F_{16}	312.	$CH_2=C(CH_3)COCl$
261.	C_6H_5F	322.	CH_3COCl
262.	$SiCl_4$	323.	C_6H_5COCl
		324.	CH_3COBr

relation equation (i.e. the index of the found temperature in the temperature array) and the value of the found temperature or the arrays with the indexes of the correlation equations and corresponding temperatures, if there was more than one of them.

Due to the structure of the program, the calculation of the ordered rate or equilibrium constant (constants) according to found correlation equation (equations) and the print of the corresponding part of the final results are accomplished immediately after the search of each temperature. Then the next ordered value of the temperature is searched etc. If the same calculations are to be executed for various temperature values (e.g. there are the data at one single temperature for the ordered reaction, only), these calculations as well as the print of the results is not repeated.

After the calculations and the print of results for all temperature values, follows the move-in of the KCC. The further operations depend on its value.

References

1. T.J. Jüriado, Organic Reactivity, 21, 375 (1984).
2. Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions. Vol. 5(II), VINITI, Moscow, 1979.

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PROGRAM PACKAGE FOR COMPUTER STORAGE AND AUTOMATIC SEARCH OF CORRELATION EQUATIONS AND FOR CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS. 4. ALGORITHM FOR CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS ON THE BASIS OF RESULTS OF REACTION SET SEARCH. SHORT MANUAL OF PROGRAM USE.

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The algorithm of the final segments executing the analysis of note codes, the search and calculation of substituent constants, the calculation of rate or equilibrium constants and some other actions are presented. In the Appendix, a Short Manual for move-in of the input data illustrated with an actual example and an example of the print of results is given.

The segments of the reaction set search described in two previous papers[1,2] gave as a final result the values for constants and array items which are used in the final parts of the program - in the segment of the analysis of note codes, of the search and calculation of substituent constants /SC/ and of the calculation of rate or equilibrium constants according to correlation equations as well as in the segment of the print of final results.

From the results of the segments of the reaction set index search on the basis of reaction and substituent codes, those are the rule code for calculating the substituent constants /RCCC/ and constants which determine the type of the connectivity of the ordered substituents to those from the

identification array with a variable secondary substituent /VSS/. The latter constants called below the connectivity information include the code of the terminal bridge, the index of VSS according to the system given in paragraph 4 of Ref. 3, the ordered codes of secondary substituents /CSS/ connected to the VSS of the array of the arrangement of coincidence and connectivity /AAS/. The solvent search program transfers the information to the final segments by the value of parameter called the indicator of the coincidence type of the ordered solvent /ICTS/. If the ICTS is less than zero, the solvent is one of the variable factors in the equation used for final calculations and the index of the found solvent /IFS/ is needed to complete these calculations. From the results of temperature search, the index (call number) of the correlation equation /ICE/ is the most essential one. If the temperature acts as a variable factor in the final equation, the ordered value of temperature /T/ is used, too.

The main routine controles the segment work with the value of the parameter of the repeated call /PRC/. In many cases the calculations of ordered constants are performed according to some alternative equations. In case of the repeated call of the calculation segments, the PRC is equated to a certain value and a part of the segment is omitted.

Besides the calculated values of the ordered constants, the segment actions also provide information for printing block, including the type indexes of the equation coefficients, the note codes etc.

Below, the main actions of the program segment are presented.

1. The Determination of Codes and Indexes from the Array of Combined Codes.

The segment work begins with the unpacking of the combined codes of the correlation equation /CCCE/. The CCCE are inserted into the one-dimensional array, the item indexes of which correspond to the indexes of the correlation equations (i.e. the indexes of temperature array /TA/, see Ref. 2) and is generally decoded as

$$CCCE = NC \cdot 10^7 + ICT \cdot 10^5 + CICE,$$

where NC, ICT and CICE denote the combined index (or code) of the note, the type index of rate or equilibrium constant and the combined index of the correlation equation, respectively. The NC structure is presented in paragraph 4. For the ICT, the following values are accepted (for details see "Tables"[4]):

1 pK_A

2 pK_B

3 lgk_A

4 lgk_{AB}

5 lgk_{AC}

6 lgk_{BC}

7 lgk_{ABC}

8 lgk_A/lgk_H

9 lgk_B

The ICT value is used to control the printing. The CICE is formed as

$$CICE = NPCE \cdot 10^4 + ICE,$$

where NPCE and ICE are the parameter number of the correlation equation in the array of equations with NPCE parameters.

2. The Check and Rearrangement of the Substituent Codes in the Connectivity Information Array.

The number of variable substituents as the factors of the correlation equation (the number of ordered substituents connected to the substituents of the identification array) is determined by the items of the connectivity information array. If the number is greater than unity, the accordance of the arrangement of the connected substituents in the array of the coincidence arrangement AAS to the arrangement of the correlation equation terms corresponded to variable substituents is checked. The rearrangement of the AAS items and the calculation of the rule code corrected value for calcu-

lating the substituent constants /RCCC/ is carried out, if required.

3. The Correction of the Position Indexes of the Secondary Substituents Connected to the Variable Secondary Substituents of the Identification Array According to the RCCC.

The correction is needed for the unified use of the constants for meta- and para-substituents in all aromatic cycles in the cases when an aromatic cycle functions as the terminal bridge, provided that the position numbers of the cycle do not begin with the free valency (heterocycles , 2-naphthyl). In such cases, the RCCC has value 2,3,4, or 5.

4. The Analysis of Notes and the Determination of the Value of the Control Constant for Note Printing.

The combined index of the note /NC/ determined from the combined codes of the correlation equation can have the following values:

a) NC = 0 - there are no notes to given equations;

b) $0 < NC < 100$ - the direct digital code of the note. The notes are used to specify the compound structure (cis-trans--isomers, threo- and erythro-compounds), reaction conditions or experimental methods etc. The bulk of the information needed by a user is printed in the final results according to the value of the control constant for note printing;

c) $NC > 100$ - the address of the combined code of the note /CCN/ in the array of the CCN

$$CCN = NN \cdot 10^3 + BAN,$$

where NN is the number of notes to the given equation and the BAN is the base address of them in the note array /NA/.

The NA is used for information storage in two cases:

- there is more than one note, connected with the correlation equation;

- the correlation equation has one or more alternatives, i.e. the data are correlated according to two or more different but indistinguishable in the sense of the adequacy equations. In this case, there are the combined codes of alternative equations /CCAE/ in the note array

$$CCAE = NC \cdot 10^5 + CICE$$

The NC and CICE for the alternative equations are given via the common field to the main routine and are used after the calculation of the ordered constant according to the main equation.

5. The Unpacking of the Type Indexes of the Equation Coefficients, the Assignment of Coefficients.

The type indexes of the equation coefficients /TIEC/ are given in Table 1. The Table includes the codes for those coefficients, only, which are actually presented in the arrays. The index indicates the sequence number of the variable substituent. Letter α presents the coefficient of the temperature parameter ($10^3/T$), the symbols like $c_{(10^3/T)\cdot\delta^{\pm}}$ indicate the coefficients of cross terms ($(10^3/T)\cdot\delta^{\pm}$ etc.).

Table 1.

1.	φ°_1	28.	ω
2.	φ°_2	29.	δ
3.	$\varphi^{+}_{R(1)}$	30.	δ°
4.	$\varphi^{+}_{R(2)}$	36.	$c_{(10^3/T)\cdot\delta^{\pm}}$
5.	$\varphi^{-}_{R(1)}$	41.	b
6.	$\varphi^{-}_{R(2)}$	42.	e
7.	$c_{\delta^{\circ}_1\cdot\delta^{\circ}_2}$	43.	p
15.	α	44.	y
16.	$c_{(10^3/T)\cdot\delta^{\circ}_1}$	45.	$c_{B}\cdot\delta^{\circ}$
17.	$c_{(10^3/T)\cdot\delta^{+}_{R(1)}}$	46.	$c_{E}\cdot\delta^{\circ}$
18.	$c_{(10^3/T)\cdot\delta^{-}_{R(1)}}$	47.	$c_{P}\cdot\delta^{\circ}$
26.	φ^{*}	50.	$c_{E}\cdot\delta^{+}$
27.	h	51.	$c_{P}\cdot\delta^{+}$

The TIEC are packed into arrays separately for single-, two-, three- and other multiparameter equations. Every item of the array for single-parameter equations includes the coefficient codes of four equations and the items of two--parameter equations - the codes of two equations. In every item of the arrays for three- and four-parameter equations, there are the coefficient codes for one equation. In the arrays for equations with more parameters, the coefficient codes for one equation occupy two items of the array following one after another.

The coefficients of correlation equation /CCE/ are also inserted into separate arrays according to the number of parameters. For the coefficients of uni-parameter equations, there are two array items for every equation (the odd items corresponding to the absolute term, the even items to tthe coefficients). For every two-parameter equations, there are three items in the array, etc.

After the unpacking of TIEC, the values of TIEC and CCE are assigned to the items of two auxiliary arrays.

6. The Search and Calculation of Substituent Constants, the Search of Solvent Constants.

The substituent /SC/ and solvent constants /SoC/ are inserted into following arrays:

a) the array of the constants for functional groups and substituents equated with them. This array includes the σ^* and φ-constants for the substituents mentioned as well as for those of the $CX_{i(i=1,n)}H_{3-n}$ type which have direct digital codes in Table 4, Ref. 3. The line index is found by means of the auxiliary array whose items are the digital codes of the substituents and the items indexes correspond to the indexes of the array of substituent constants;

b) the array of the constants for alkyl substituents includes σ^*, E_s, E_s^0 and φ-parameters. The indexes of the first fifty lines are equal to the substituent codes in table 4 of Ref. 3. For the rest of the substituents, the indexes are determined by a special segment;

c) the array of the constants for the $CX_{i(i=1,n)}H_{3-n}$

type substituents includes σ^{*}, E_s, E_s^o and φ-parameters. The line index is determined by means of two auxiliary arrays;

d) two arrays of the constants for meta- and para-substituted phenyls. The arrays include σ^o for meta- and σ^o, σ_R^+ and σ_R^- for para-substituted phenyls, respectively. Both arrays are supplemented with an auxiliary array to determine the line index;

e) the array of solvent constants. It includes the polarity /Y/ and polarizability /P/ constants and the parameters of general acidity /E/ and general basicity /B/ and has also one auxiliary array.

The input data for the SoC search are the type indexes of the equation coefficients /TIEC/, for the search of the SC besides the TIEC the rule code for calculating the substituent constants /RCCC/ as well as the connectivity information.

Besides the values given in paragraph 3 (2,3,4 or 5), the RCCC can have the following values:

- RCCC = 0 - the hydrogen is connected to the variable secondary substituent /VSS/ of the identification array;
- RCCC = 1 - a direct search of the SC from the arrays or the direct adding up of constants for secondary substituents;
- RCCC = 10 - the calculation of the SC for an alkyl substituent connected to the VSS of the type of functional groups;
- RCCC = 11 or 12 - the calculation of the SC for an alkyl substituent consisting of one or more methylene bridge(s) and 1-3 (alkyl) secondary substituents;
- RCCC = 21 - the calculation of the SC of the $CX_{i(i=1,n)}H_{(3-n)}$ type using the SC for substituents X;
- RCCC = 22 - the same for the $CX_{j(j=1,m)}H_{2-m}X_{i(i=1,n)}H_{3-n}$ substituents.

In principle, the calculation (or at least an approximate estimation) of the SC is at present possible for the σ^{*} and φ, only. Therefore, the limitation mentioned in 2,4.,Ref.3 according to which the secondary substitution is acceptable

at the terminal bridge, only, ie not essential in the case of correlation approach.

The calculating formula for [5]:

- for RCCC = 11-12

$$\delta^{*}_{summ.} = -0.49 + 0.204 \cdot \sum_i \delta^{*}_i$$

- for RCCC = 21

$$\delta^{*}_{summ.} = -0.49 + 0.4 \cdot \sum_i \delta^{*}_i$$

- for RCCC = 22

$$\delta^{*}_{summ.} = -0.49 + 0.4 \cdot \sum_i \delta^{*}_i + 0.4^2 \cdot \sum_j \delta^{*}_j$$

The formula for [6]:

$$\varphi_{CX_1X_2X_3} = 3.94 - 0.200(\varphi_{X_1} + \varphi_{X_2} + \varphi_{X_3}) + 0.020(\varphi_{X_1}\varphi_{X_2} +$$

$$+\varphi_{X_1}\varphi_{X_3} + \varphi_{X_2}\varphi_{X_3}) - 0.002\varphi_{X_1}\varphi_{X_2}\varphi_{X_3}$$

The values of the SC and SoC obtained are assigned to the items of the corresponding auxiliary array.

7. The Calculation of the Ordered Rate (Equilibrium) Constant.

The calculation of the ordered constants is carried out using the coefficients of correlation equations /CCE/ found from the corresponding arrays and the found or calculated SC and SoC. The present version of the program is parameterized on the basis of "Tables of Correlation Parameters" published in[5]. Our system guarantees the replacement of those equations with more general correlation equations or with equations based on other principles (e.g. on some physical models) without changes in the segments of the reaction set search, if the mentioned equations are formed on the same grounds as correlation equations (i.e. the reaction sets with one or more variable secondary substituents are regarded). In such cases, a number of reaction sets can be included in one equation.

8. The Calculation of the Ordered Rate (Equilibrium) Constant According to an Alternative Equation.

The calculation of the constant according to an alternative equation differs from those according to the main equa-

tion. Namely, the procedures described in paragraphs 1,2,3 and 4 are omitted, but the type indexes of the equation coefficients /TIEC/ and SC (SoC) found in the first stage of the calculations are added to the items of the auxiliary array. If the new value of the TIEC coincides with the previous one, the search (calculation) of the SC (SoC) is omitted and the values obtained earlier are used.

As in other segments, various messages about failures and errors may occur in the course of actions of the described segment.

Appendix

Short Program User's Manual

1. Move-in of Input Data.

The input data are moved in from the punch cards* the pack of which has the following structure:

- the initial card of the next move-in (ICNM);
- the card with the general form of the reaction code (see paragraph 3 Ref. 3) in the I8, I4 format;
- the card with the ordered number of variable substituents (see the Flow Chart in Ref. 1) in the I4 format;
- the cards with the substituent codes in the I5 format; on every card, there is one bridge code, one code of secondary substituent or a closing symbol ;
- the ICNM;
- the cards (from one to three) with the solvent codes (see in Ref. 2) in the 14 (the first card with the index of the first compound) or in the I4, F6.3, I3 format (the second and third one, with the index, concentration and its dimension index of the second and third compound).

Note:

It is recommended to order binary and ternary solvents always in mole per cents (i.e. ICD = 0, see Ref. 2); except for the cases, when the messages to the earlier executed orders indicate the presence of data for somewhat different concentration dimension;

* When using the computer with other types of terminals (interactive ones), the dialog move-in can be used. Thus, in general, the entry is kept in view when speaking about punch card.

- the ICNM;

- the cards (from one to three) with the temperature value (values) in the F6.3 format;

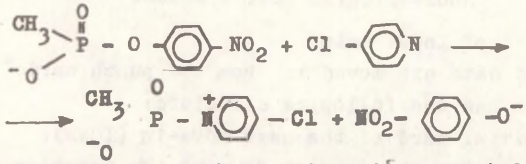
- the ICNM;

- the card with the continuation constant /KCC/ (see the Flow Chart in Ref. 1) in the I2 format.

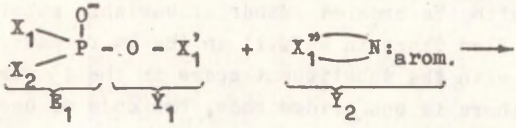
The move-in of some further data depends on the KCC value as cited on the Flow Chart in Ref. 1.

2. Example of Move-in of Input Data.

The rate constant for the following reaction in water, at 25°C is ordered:



The general form of the reaction is presented as



X_1 (CH_3)	-1	2	-1		
X_2 ($-O^-$)	-1	58	-1		
X_1' ($-C_6H_4-NO_2$)		3	-1	4105	-1
X_2'' ($-C_6H_4-Cl$)		6	-1	4054	-1

The punch card pack of the input data:

```
//GO.FT05F001 DD
27250022   0
   4
  -1
   2
  -1
  -1
  58
```

```
  -1
   3
  -1
4105
  -1
   6
  -1
4054
  -1
//GO.FT05002 DD
   1
//GO.FT05003 DD
  25.0
//GO.FT05004 DD
 0
```

3. Print of Results.

Results are printed in two parts. The coded user's order and the search results (either positive or negative) are printed after the conclusion of the reaction set search on the basis of both reaction and substituent codes. When completing the calculation of the value of the ordered constants, the solvent order, the ordered value of temperature and the search results are printed. The search results consist of the code of the solvent found, the temperature value (including the temperature interval when using the equation with the temperature as a variable factor), the type and value of the constant, the type of the correlation equation used for the calculation of the constant (the codes presented in Table 1 are used) and messages (notes), as a rule, in decoded form (exceptions are e.g. the codes of solvents whose data were used to compose the correlation equation with the solvent as a variable factor).

4. Example of Results Record.

The results record for the order given in paragraph 2 is presented in Table 2.

For technical reasons, the record is given in some disfigured (compressed) form.

The versions of negative results are described in the

Table 2

Example of Results Print

ЗАКАЗАНО	НАЙДЕНО
КОД РЕАКЦИИ 27250022 0	ТИП РЕАКЦИИ 80 ИНДЕКС РЕАКЦИИ 641
MSI (1) -1 2 -1	MRI (1) -1 2 -1
MSI (2) -1 38 -1	MRI (2) -1 58 -1
MSI (3) 3 -1 4105 -1	MRI (3) 3 -1 4105 -1
MSI (4) 6 -1 4054 -1	MRI (4) 6 -1 -1 -1

ЗАКАЗАНО		НАЙДЕНО				
Среда	Темп.	Среда	Темп.	Константа	Уравнение	Примечание
1	40,0	1	60.0	LGK(AB)= -6.26	1 + 3	

corresponding parts of the previous papers[1,2].

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KINETICS OF INTERACTION OF α-HALOGENDESOXYBENZOINES WITH ALIPHATIC AMINES. 1. STRUCTURE EFFECT OF AMINE.

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Reaction kinetics of α-bromodesoxybenzoine with aliphatic amines has been studied at 25°C. It has been found that the interaction mechanisms of primary and secondary amines differ from those of tertiary ones. It was established that sterically hindered amines ($E_N \leq -3$) do not form any products of nucleophilic substitution reactions with α-bromodesoxybenzoine.

The reactions of α-haloketones, those of α-bromodesoxybenzoines (desylhalogenides) in particular, with various nucleophiles have been studied widely enough[1,2]. Nevertheless, the kinetic side of aliphatic amines constituting a good model for establishing the effect of nucleophile reagents' structure on the rate and formation mechanism of aminoketones, has not been thoroughly examined yet. The present paper deals with the problems of the interaction of aliphatic amines belonging to different classes (primary, secondary and tertiary) with α-bromodesoxybenzoine in benzene. Analysis of kinetic regularities and specification of the formed products show that the α-bromodesoxybenzoine reactions with primary and secondary aliphatic amines (as it was in case of aromatic amines[3]) proceed quantitatively and irreversibly according to the following scheme:

$$ArCOCHBrAr + 2NHR_1R_2 \longrightarrow ArCOCH(NR_1R_2)Ar + R_1R_2\overset{\oplus}{N}H_2 \cdot \overset{\ominus}{Br}, \quad (1)$$

With such tertiary amines as trimethyl- and dimethylbutylamines the reaction proceeds as follows:

$$ArCOCHBrAr + NR_1R_2R_3 \longrightarrow ArCOCH(\overset{\oplus}{N}R_1R_2R_3)Ar \cdot \overset{\ominus}{Br} \quad (2)$$

With diisopropyl, diethylmethyl- and triethylamines in which the nitrogen atom is heavily screened with hydrocarbon radicals, the process proceeds in a more complicated way. Thus, e.g. in case of reactions of triethylamine with desylbromide instead of the expected triethylammonium desylbromide were obtained diphenyldiketone (ArCOCOAr), and salt of the hydrobromic acid of the initial triethylamine. The residue was a mixture consisting of different compounds, difficult to identify (for details, see Experimental). Diisopropyl- and diethylmethylamine act analogously. We did not undertake a detailed study of the reaction mechanism in case of the above-mentioned amines, although this interaction seems to have certain specific features arising from the amine structure. Evidently, here the proton detachment from the α-carbon atom of the substance takes place which is followed by various changes leading to the formation of the carbanion[4].

For the majority of amines studied (Table 1) α-aminoketones and their salts (Eqs.(1) and (2)) are formed during the reactions. Their rates are described by second order reactions (the first for each separate reagent).

Sometimes (see 1,4,6,10) together with the mentioned bimolecular process the other reaction channel catalyzed by the second molecule of the initial amine can be observed*. In such a case rate constants of noncatalytic (k) and catalytic (k_b) reactions were found according to linear dependence of $k_{obs.}$ on b (b - amine concentration).

Comparison of the k values (Table 1) shows that reactions of α-bromodesoxybenzoine with aliphatic amines are

* The mentioned catalysis is not observed with all amines and its effect is quite insignificant (ratio k_b/k varies from 2.3(10) to 6.5(1)), for that reason it is difficult to draw any definite consequences concerning the dependence of values k_b on the structure of amines.

rather sensitive towards the structures of the latter. Thus, the drop of the rate cá 200 and 40 times, respectively, in case of passing transition from n-butyl to tertiary - butylamine (Cf. 3 and 5) and from piperidine to diethylamine (Cf. 10 and 7) are caused by the increase of spatial screening of the reaction center. Steric effects of amine structure in the present reaction, similarly with other aminolysis [5,6] processes lead to the situation where no actual relationship

Table 1

Rate Constants of α-brome Desoxybenzoine Reaction with Amines in Benzene at 25°C

No	Amine	$k \cdot 10^4$ $l \cdot mol^{-1} \cdot c^{-1}$	$k_b \cdot 10^2$ $l^2 \cdot mol^{-2} \cdot c^{-1}$
1.	methylamine	5.51 ± 0.27	0.357 ± 0.003
2.	ethylamine	5.22 ± 0.05	
3.	n-butylamine	5.20 ± 0.07	
4.	iso-propylamine	0.683 ± 0.008	0.0374 ± 0.0002
5.	tert-butylamine	0.0272 ± 0.0008	
6.	dimethylamine	45.8 ± 1.4	3.04 ± 0.13
7.	diethylamine	1.14 ± 0.02	
8.	di-n.-butylamine	1.39 ± 0.02	
9.	diisobutylamine	0.673 ± 0.07	
10.	piperidine	42.5 ± 0.4	0.987 ± 0.04
11.	trimethylamine	1.85 ± 0.11	
12.	dimethylbutylamine	0.243 ± 0.004	

between the nucleophilicity and basicity of the studied compounds was not detected.

Attention should also be called to the change of the reactivity of amines belonging to different classes. Thus, the transition from methylamine to dimethylamine (cf. 1 and 6) is accompanied by cá 8-fold increase of the process rate, while during the transition from dimethylamine to trimethylamine (6 and 11) the rate markedly drops (cá 25 times). For phenacylbromide[5] and trans-p-nitrophenyl-ß-chlorovinylsulphone[6] reactions the acceleration of the process during

the transition from methylamine to dimethylamine is greater (ca 13 and ~ 380 times, respectively), but the rate decrease in case of trimethylamine is negligible (1.6 and 1.3 times, respectively).

One can suppose that α-bromodesoxybenzoine interaction with the primary and secondary amines on the one hand and with the tertiary amines on the other hand is carried out differently from the analogous reactions of phenacylbromide and trans-p-nitrophenyl-ß-chlorovinylsulphone . For the latter a common mechanism with amines of various classes[5,6] has been established earlier.

In order to quantitatively evaluate the effect of amine's structure on the reaction rate studied the following equation was used[7]:

$$\log k = \log k_0 + \rho^{*}\Sigma\sigma^{*} + \delta E_N, \qquad (3)$$

where $\Sigma\sigma^{*}$ denotes the inductive substituent effect at the nitrogen atom, E_N is the steric effect of amine molecule, ρ^{*} and δ denote the reaction series sensitivity to the corresponding effect.

For the primary and secondary amines the equation is:

$$\log k = (0.28\pm0.49) - (3.62\pm0.53)\,\Sigma\sigma^{*} + (1.62\pm0.18)E_N \quad (4)$$

$$(s = 0.31;\ R = 0.958;\ N = 10)$$

If the rate constant for tert.-butylamine* is not taken into consideration, the correlation becomes remarkably better:

$$\log k = (-0.34\pm0.29) - (2.91\pm0.32)\,\Sigma\sigma^{*} + (1.35\pm0.11)E_N \quad (5)$$

$$(s = 0.16;\ R = 0.980;\ N = 9)$$

The inclusion also of the results for the tertiary amines (11, 12 Table 1) evidences about the lack of correlation:

$$\log k = (-1.14\pm0.69) - (1.92\pm0.71)\,\Sigma\sigma^{*} + (1.34\pm0.31)E_N \quad (6)$$

$$(s = 0.56;\ R = 0.828;\ N = 12)$$

*Exclusion of tert.-butylamine results in better correlation parameters of eq.(3) for relations of aliphatic amines with 2.4-dinitrochlorobenzene and methyl bromide[7].

Such a significant worsening of correlation parameters in case of introducing tertiary amines may be caused by various reaction mechanisms for these amines on the one hand, and for the secondary ones on the other hand.

If the reaction mechanism for amines belonging to different classes[6,8] is supposed to be the same, their reactivity obeys equation (3)[5,6].

As it has already been mentioned, the behavior of sterically hindered amines (diethylmethylamine E_N= -3,0[7]; triethylamine, E_N= -3.8[5]; diisopropylamine, E_N= -3.90[7]), in the reactions mentioned, is anomalous. Consequently, the aliphatic amines interact with α-bromodesoxybenzoine according to eqs. (1) and (2) only if the reaction center in amine has a certain level of steric accessibility, when $E_N > -3$. A different way of conversion of tertiary amines can be explained with the existence of the hydrogen atom at the primary and secondary amines and its participation in the transition stage. Interaction kinetics of piperidine and N-deuteropiperidine with α-bromodesoxybenzoine and phenacylbromide in acetonitrile** at 25°C (Table 2) was studied in order to check the above suggestion. Relation k_H/k_D,

Table 2

Rate Constants of α-Bromodesoxybenzoine and Phenylbromide Reactions with Piperidine (k_H) and N-Deuteropiperidine (k_D) in Acetonitrile at 25°C.

Compound	k_H, 1 mol^{-1} · c^{-1}	k_D, 1 mol^{-1} · c^{-1}	k_H/k_D
α-bromodesoxybenzoine	0.93 ± 0.01	0.737 ± 0.009	1.27 ± 0.02
phenacylbromide	5.31 ± 0.06	5.90 ± 0.05	0.90 ± 0.01

** The absence of catalytic flow conditioned the use of acetonitrile as the solvent.

being the qualitative measure of hydrogen isotope effect, is smaller than unity in case of phenacylbromide.

Approximate value of kinetic isotope effect (0.86) has been observed for reactions of this compound with aniline and N,N-dideuteroaniline in nitrobenzene [9]. In our case, the α-bromodesoxybenzoine reaction rate is greater on the contrary with piperidine that with its deuterated analogues. The existence of this, though insignificant, primary isotope effect shows that the proton transfer proceeds at the rate of the determining step. With tertiary amines containing no hydrogen such a phenomenon is impossible.

Thus, the obtained data allow to come to the conclusion that reaction mechanisms for primary and secondary amines on the one hand and those for tertiary ones on the other hand are different.

Experimental

The amines and the solvents were purified according to the known methods. α-bromodesoxybenzoine was synthesized and purified as described in [10]. N-deuteropiperidine was isolated from piperidine by the method of change for D_2O [11]. The hydrogen change level for deuterium was checked by the IR-spectrum [9]. It was established that the deuterification of piperidine could be observed within the range of cā 90 per cent. The solutions were prepared and the experiments with N-deuteropiperidine were conducted under dry box conditions.

Kinetic measurements were carried out under pseudomonomolecular conditions at a remarkable excess of amine (up to 70-90% of substance transformation. The process was controlled by the formation of halogenide ions which were determined by argentometric titration.

While applying acetonitrile as a solvent, the process was controlled either spectrophotometrically (according to α-bromodesoxybenzoine consumption, λ = 266 nm) or conductometrically (in accordance with the accumulation quantity of the hydrogen bromide of amine salt obtained in the

course of the process). All these methods lead to practically identical results.

The second order rate constants were calculated according to the ordinary formula, while b = const, taking into consideration the mean value of 2-3 parallel runs. The accuracy of the obtained date was evaluated and the correlation parameters were calculated by means of mathematical statistics.

Separation of Reaction Products. In most cases with the quantitative yields (95-98%) were obtained aminoketones or their chlorohydrates (Table 3, 1-6) as described below.

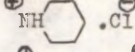
After the reaction between the primary or secondary amines and α-bromodesoxybenzoine in benzene, the reaction mixture was washed in 2% hydrochloric acid, water, in 2% solution of caustic soda and again in water. Benzene solution was carefully treated with steam after drying with anhydrous sodium sulphate. The residue was aminoketone. As forming of aminoketones tended to be rather unstable, in some cases their chlorohydrates were obtained by means of conducting dry hydrogen chloride into benzene solution of aminoketone and by the further cristallization of salt from alcohol. For trimethylamine and dimethylbutylamine the reaction residue was filtrated, washed in anhydrous ether and then dried in vacuo (Table 3; 7,8). By the elemental analysis and the NMR spectra it was established that similarly with piridine[13], these salts cristallize in the form of benzene complexes. While treating the benzene complex of trimethylammoniumdesylbromide with the picric acid residue in ethanole stable picrate was isolated with a melting point being 218-219°C. % found: C 57.61; H 4.79; N 11.88. $C_{23}H_{22}O_8N_4$. % calculated: C 57.22; H 4.60; N 11.61.

Products of α-Bromodesoxybenzoine Reaction with Triethylamine.

The mixture consisting of 1.5 g of α-bromodesoxybenzoine and 2 ml triethylamine in 50 ml of dry benzene was kept for 20 days. The sediment obtained (0.6 g) was crystallized and identified as hydrobromic salt of triethylamine.

Table 3

Character of $(C_6H_5COCH(R)C_6H_5)$ Products of α-Bromodesoxybenzoine Reaction with Aliphatic Amines

No	R	Melting T°C exp.	Melting T°C ref.	Found % C	Found % H	Found % Hal	Found % N	Brutto formula	Calculated % C	Calculated % H	Calculated % Hal	Calculated % N
1	$\overset{\oplus}{N}H_2CH_3.\overset{\ominus}{Cl}$	216-220	216-220 I2									
2	NHC_2H_5	208-209 a)		80.41	6.78		5.93	$C_{16}H_{17}NO$	80.30	7.16		5.85
3	$NHC(CH_3)_3$	93-94		81.80	7.60		5.59	$C_{18}H_{21}NO$	80.86	7.91		5.24
4	$\overset{\oplus}{N}H(CH_3)_2.\overset{\ominus}{Cl}$	231-233		69.65	6.43	12.76	5.19	$C_{16}H_{18}ClNO$	69.69	6.58	12.86	5.08
5	$\overset{\oplus}{N}H(C_2H_5)_2.\overset{\ominus}{Cl}$	185-188	184-188 I2									
6		240-242	239-242 I2									
7	$\overset{\oplus}{N}(CH_3)_3.\overset{\ominus}{Br}.C_6H_6$	80-97		66.53	6.55	19.61	3.80	$C_{23}H_{26}BrNO$	66.99	6.34	19.40	3.40
8	$\overset{\oplus}{N}C_4H_9(CH_3)_2.\overset{\ominus}{Br}.C_6H_6$	145-146		68.73	7.27	17.54	3.57	$C_{26}H_{32}BrNO$	68.59	7.25	17.57	3.07

a) Melting point of chlorine hydrate.

Benzene was distilled off the filtrate without heating under vacuo. After that, the extraction (three times, 10 ml each) by cyclohexane* was carried out; the solvent was distilled while the product consisting of yellow crystals (0.7 g) was actually diphenyldiketone.[14]

Products of α-bromodesoxybenzoine Reaction with Diisopropylamine.

The mixture consisting of 2 g of α-bromodesoxybenzoine and 2.88 g of diisopropylamine in 40 ml of acetonitrile was kept at room temperature for 18 days. Then acetonitrile and the excess of diisopropylamine were distilled under vacuum without heating. The residue was treated with cyclohexane (30 ml) and identified as hydrobromic salt of diisopropylamine. The attempts to determine the composition and structure of the products failed.

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* Resinous mixture of indistinguishable compounds was obtained after the extraction.

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KINETICS OF INTERACTION OF α-HALOGENDESOXYBENZOINES WITH ALIPHATIC AMINES. 2.EFFECTS OF MEDIUM, TEMPERATURE AND NATURE OF SUBSTRATE LEAVING GROUP

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The effect of medium, amine structure, the nature of the substrate leaving group and temperature on the rate of α-halogendesoxybenzoine reactions with aliphatic amines has been studied.

It was concluded from the analysis of the obtained data that the process mechanism in case of primary and secondary amines differ somewhat from that for the reactions of tertiary amines. At the same time the breaking of the carbon-halogen bond turned up to be the rate determining stage for all reactions studied. In transition stage the extent of the bond rupture is practically identical.

In the previous paper [1] it was shown that α-bromodesoxybenzoine reactions with primary and secondary amines in benzene on the one hand and with tertiary amines, on the other hand, have different reaction mechanisms. In order to clarify the other general regularities and pecularities of these processes, the present study is aimed at establishing the influence of the medium, the nature of the leaving group and temperature on the reaction rate.

The experimental results showed that both in acetonitrile and in benzene[1] the reaction rate can be described by the second order equation (the first order for each reagent).

The comparison of obtained values of k (Table 1) indicates that the amines' reactivity is highly dependent on their structure. As in benzene[1], the structure effect of primary and secondary amines on their activity can well be described with eq. (1), suggested earlier[2], which takes into consideration the induction effect of the radicals at nitrogen atom ($\Sigma \sigma^*$) and the steric effect of the amine molecule (E_N):

$$\log k = \log k_o + \rho^* \Sigma \sigma^{*\prime} + \delta E_N \qquad (1)$$

The data from Table 1 was treated according to the equation (without tert.-butylamine); resulting in the following relationship:

$$\log k = 2.03 \pm 0.26) - (2.89 \pm 0.28) \Sigma \sigma^* + (1.48 \pm 0.11) E_N$$

$$(s = 0.17;\ R = 0.980;\ N = 11) \qquad (2)$$

The comparison of the corresponding coefficients for reactions in acetonitrile and benzene[1], where $\rho^* = 2.91 \pm 0.32$ and $\delta = 1.35 \pm 0.11$ refers to the fact that the solvent polarity has practically no effect on the susceptibility of the series under discussion to either the inductive (ρ^*) or the steric (δ) effects of the amine.

Inclusion of tertiary amines (trimethylamine and dimethylbutylamine) into the general comparison leads to (eq. (3)) the significant worsening of the correlation (cf. values s and R in eqs. (2) and (3)). It agrees with the earlier[1] made conclusion about the reaction mechanism differences between α-bromodesoxybenzoine:

$$\log k = (0.74 \pm 0.66) - (1.31 \pm 0.67) \Sigma \sigma^* + (1.22 \pm 0.31) E_N$$

$$(s = 0.51;\ R = 0.82);\ N = 13) \qquad (3)$$

Table 1

Rate Constants of α-Bromodesoxybenzoine Reactions with Amines in Acetonitrile at 25°C

No	Amine	$k \cdot 10^{-2}$, $l \cdot mol^{-1} \cdot c^{-1}$
1	methylamine	19.6 ± 0.1
2	ethylamine	7.68 ± 0.02
3	isopropylamine	1.18 ± 0.01
4	butylamine	8.36 ± 0.03
5	tert.-tributylamine	0.0683 ± 0.0007
6	cyclohexylamine	2.18 ± 0.01
7	dimethylamine	108 ± 1
8	diethylamine	1.67 ± 0.02
9	methylpropylamine	19.1 ± 0.01
10	di-n-butylamine	2.00 ± 0.01
11	diisobutylamine	0.731 ± 0.002
12	piperidine	93 ± 1
13	trimethylamine	2.06 ± 0.04
14	dimethylbutylamine	0.219 ± 0.002

and the amines of various classes.

The direct comparison of reaction rate constants including all amines in acetonitrile (Table 1) and benzene[1] has demonstrated the existence of a good correlation between them (s = 0.17, r = 0.985).

The situation reminds that of α-bromoketone phenacylbromide[3] reactions, where the similar mechanism for reactions with primary, secondary and tertiary amines[3,4] holds. In a number of papers (see e.g.[5]) the supposition has been made that the linearity of log k values of the given and standard reaction series refer to the same type of the reactions. According to this, the dependence found refers to the identical interaction types of α-bromodesoxybenzoine with amines of different classes. But our data prove that such a conclusion can be drawn only after a great number of thorough studies

and data comparison.

Thus, the effects of various solvents on the ratio of the reactivity of nitrogen with an hydrogen atom (dimethylamine) and those without (trimethyl) amines in reactions with phenacylbromide and α-bromodesoxybenzoine (Table 2) have different expression. In the first case where the reaction mechanism for any amine is presumed to be the same, the transformation from dimethylamine to trimethylamine is in all solvents accompanied by an insignificant and almost equal rate decrease (1.6 - 2.9 times). But as to α-bromodesoxybenzoine reactions, the changes in absolute value are more substantial (9 - 60 times) depending on the medium characteristics.

Table 2

Reaction Constants $k \cdot 10^2 (l \cdot mol^{-1} \cdot c^{-1})$ of Phenacylbromide and α-bromodesoxybenzoine Reactions with Dimethyl and Trimethylamines in Various Solvents at 25°C

Solvent	Amine	Phenacylbromide	α-Bromodesoxybenzoine
benzene[1,4]	dimethylamine	5.02 ± 0.04	0.458 ±0.014
	trimethylamine	3.15 ± 0.06	0.0185 ±0.0011
acetonitrile	dimethylamine	333 ± 5	108 ±1
	trimethylamine	160 ± 1	2.06 ±0.04
dioxane	dimethylamine	20.7 ± 0.3	1.97 ±0.04
	trimethylamine	7.18 ± 0.09	0.0331±0.0005
methanol	dimethylamine	6.61 ± 0.08	1.60±0.02
	trimethylamine	3.57 ± 0.03	0.174±0.002

Consequently, the relations of reaction mechanisms of α-bromodesoxybenzoine with the named amines are more complicated than those of phenacylbromide. At the same time the leaving group effect on the reaction rate studied (Table 3) does not actually depend on the amine structure. Values γ denoting the susceptibility to the leaving group effect were greater than those of some other α-halogenketone reactions with amines[7]. The latter refers to the high level of looseness

Table 3

Rate Constants $k \cdot 10^2 (l \cdot mol^{-1} \cdot c^{-1})$ and Parameters of Equation $\log k = \log k_o + \gamma\tau$ [6] for Reactions of α-Halogendesoxybenzoines ($C_6H_5COCHC_6H_5$, X) with Amines in Acetonitrile at 25°C

X	Methylamine	Dimethylamine	Piperidine	Trimethylamine
Cl	0.136 ± 0.003	0.512 ± 0.005	0.671 ± 0.008	0.0131 ± 0.0002
Br	19.6 ± 0.1	108 ± 1	93 ± 1	2.06 ± 0.04
I	54.6 ± 0.2	308 ± 1	284 ± 3	6.48 ± 0.07
$\log k_o$	-7.50 ± 0.78	-7.23 ± 0.88	-6.82 ± 0.69	-8.65 ± 0.70
γ	1.38 ± 0.17	1.47 ± 0.19	1.38 ± 0.15	1.42 ± 0.15
s	0.24	0.27	0.21	0.22
r	0.993	0.992	0.994	0.994

Table 4

Rate Constants $k \cdot 10^{-2}$ ($l \cdot mol^{-1} \cdot c^{-1}$) of α-Bromodesoxybenzoine Reactions with Amines in Acetonitrile at Various Temperatures and Their Activation Parameters [b,c]

	Amine	35°C	45°C	55°C	log A	E_A, kJ/mol	$\Delta S^{\neq}$ J/mol · degree
1	methylamine	30.1 ± 0.2	40.1 ± 0.2	49.5 ± 0.6	3.7	25.0	183
2	butylamine	10.1 ± 0.1	13.3 ± 0.1	19.5 ± 0.3	2.9	22.8	198
3	dimethylamine	120 ± 2	166 ± 1	202 ± 1	3.1	17.8	194
4	di-n.-butylamine	3.11 ± 0.02	4.18 ± 0.04	5.62 ± 0.4	3.2	27.7	193
5	piperidine	107 ± 1	114 ± 1	185 ± 1	3.3	19.0	191
6	trimethylamine	2.53 ± 0.05	3.31 ± 0.04	4.15 ± 0.7	1.7	19.3	221
7	dimethylbuthyl - amine	0.405 ± 0.012	0.627 ± 0.012		4.7	42.0	163

a Values of $k_{25}°$ are presented in Table 1.

b Mean square deviations of log A, E_A and $\Delta S^{\neq}$ calculation did not exceed 0.2; 2.9 kJ/mol and 12 J/mol·degree, respectively.

c For dimethylbutylamine reactions calculated at temperatures 7° ($(7.26 \pm 0.11) \cdot 10^{-4}$ $l \cdot mol^{-1} \cdot c^{-1}$), 25°, 35° and 45°C.

of the carbonhalogen bond in the transformation state, regardless of the formation of the carbon-nitrogen bond, which should differ in the processes including the primary and the secondary amines as well as in those having the tertiary ones[1]. It was interesting to study the effect of temperature variation on the interaction rate of α-bromodesoxybenzoine with amines belonging to different classes. The corresponding rate constants and activation parameters are given in Table 4. The analysis of the latter indicates that the primary and secondary amines are characterized by the constant variation of reaction entropy (i.e. the series is an isoentropic one), which does not concern the tertiary ones. This also confirms the conjecture[1] that the tertiary amines react with α-halogendesoxybenzoines differently from the primary and secondary ones.

Experimental

The amines and solvents were purified according to the known methods. α-Chloro-[8] and α-bromodesoxybenzoines[9] were obtained and purified as described earlier, α-iodinedesoxybenzoine was synthesized via the exchange reaction from the bromoderivative. Solutions containing 5 g of bromodesoxybenzoine in 50 ml of acetone and 3.3 g of sodium iodide in 50 ml of acetone were mixed while stirring steadily. The mixture was kept at room temperature during an hour. After the filtration the solvent was removed by the vacuum distillation. The α-iododesoxybenzoine residue was repeatedly washed with water and crystallized from methanol. Melting point = 90.5 - 91.5°C. % found: C 52.15; H 3.50; I 39.62; $C_{14}H_{11}OI$. % calculated: C 52.20; H 3.44; I 39.39.

Reaction rate was measured mainly spectrophotometrically (λ =266 and 310 nm) or conductometrically under the significant amine excess. Sometimes, in order to check the abovementioned methods and also while using dioxane the potentiometric method of argentometric titration of the forming halide ion was applied.

In case of the reactions of desylhalogenides with steri-

cally hindered aliphatic amines (e.g. triethylamine and diisopropylamine) in acetonitrile various methods of the monitoring the reaction rate (either by formation of halide ion or by the consumption of the substrate) lead to the different and badly reproducible results. A mixture of several substances whose identification turned out to be impossible was obtained (see also[1]).

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KINETIC STUDY OF IONIZATION OF NITROALKANES IN MIXED SOLVENTS.IX. PHENYLNITROMETHANE AND PHENYLNITROMETHANE -d_2 IN AQUEOUS DIMETHYL SULFOXIDE AND AQUEOUS DIMETHYL FORMAMIDE

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The rate of ionization of phenylnitromethane and phenylnitromethane-d_2 has been measured in solutions of hydroxide in aqueous solvents containing 50 and 66.67 vol % dimethyl sulfoxide and 50 vol % dimethyl formamide. The activation parameters for the deprotonations and primary hydrogen isotope effects have been calculated.

In the previous papers[1,2] of this series the rates of ionization and isotope effects of nitroethane and nitroethane-d_2 in aqueous dimethyl sulfoxide and aqueous dimethyl formamide (50 vol %) were examined. It was concluded, that the accelerating effect of aprotic component is conditioned by the stabilization of the activated state. But the point for nitroethane-d_2 in aqueous dimethyl formamide deviates from the general isokinetic relationship established for the alkaline ionization of nitroethane in water and aqueous aprotic solvents. Moreover, for this medium $k^H/k^D \approx 1$. This result stimulated us to look for another analogical drastic medium effects on the kinetic isotope effects in case of phenylnitromethane.

This compound is characterized by high rates of deprotonation due to the resonance stabilization of activated state.

Experimental

Phenylnitromethane was prepared by the procedure of Kornblum[3]. The redistilled fraction bp. 53° (0.025 mm) n_D^{20} 1.5310 was additionally purified by column chromatography (solid support-acidic silica gel (100 mesh), solvent - hexane: methylene chloride (1:1). Fraction containing no more than 5% of impurities according to the check by gas chromatography, was collected.

n_D^{20} 1.5329; d_{20}^{20} 1.1585

Phenylnitromethane-d_2 was prepared by the combined procedure of Bell, Goodall and Leitch[4,5]. Rectified product had bp 91.5-92° (2 mm); n_D^{20} 1.5315; d_{20}^{20} 1.1749. Deuterium content was 97.4% (by density).

Dimethyl sulfoxide redistilled, bp 93-93.5° (20 mm) n_D^{20} 1.4772; d_4^{20} 1.1016.

Dimethyl formamide was kept under molecular sieves 4A, the rectified product had bp 68-69° (30 mm), n_D^{20} 1.4305; d_4^{25} 0.9454.

Deprotonation kinetics has been studied spectrophotometrically using the stopped flow installation described earlier[1]. The kinetical measurements were carried out under the pseudofirst order conditions at various base concentrations (0.01-0.07 M) and temperatures. After mixing in reaction cell the concentration was about 5.10^{-4}M of nitro compound. In all experiments constant electrolyte concentration (0.1M) was maintained by adding NaCl. The wave-length used for the phenylnitromethane ionization was 305 nm. The second order rate constants were calculated by the means regression in co-ordinates $k_I - [OH^-]$ * or directly from equation $k_{II} = k_I / [OH^-]$.

The second-order rate constants obtained in this study and extracted from papers[6,7], are collected in Table 1.

* As a consequence of the relatively large scattering experimental points, the systematic errors expressed by the nonzero value for intercept could not be unambiguously discussed.

Table 1.

Rate Constants for Phenylnitromethane Reaction with Hydroxide Ion and the Values of Primary Hydrogen Isotope Effect (k^H/k^D). Standard errors are given, n - number of different hydroxide ion concentrations used, M - the number of tests.

Solvent [a]	t°C	$k^H_{II}.10^3$ $M^{-1}\ s^{-1}$	n	m	$k^D_{II}.10^{-3}$ $M^{-1}\ s^{-1}$	n	m	k^H/k^D
H_2O	25	0.151±0.003[b]			0.0204[b]			7.4
	25	0.151±0.004	4	46	0.0193±0.004	4	56	7.8
50% DMSO	15	1.047[d]			0.349±0.08	5	56	3.0
	20	1.38±0.21[c]			0.467[d]			2.95
	25	1.73[c]			0.631±0.02	4	62	2.74
	30	2.08±0.22[c]	5		0.871[d]			2.38
	40	3.69±0.18[c]	4		1.584[d]			2.32
	45	4.47[d]			2.140±0.08	4	48	2.08
66.67% DMSO	15	8.51[d]			2.651±0.3	7	68	3.21
	20	10.47±1.79[c]	5		3.02[d]			3.47
	25	13.28[c]			3.50±0.4	8	89	3.85
	30	17.03±2.36[c]	5		4.37[d]			3.90
	40	24.60±0.89[c]	5		5.89[d]			4.18
	45	31.62[d]			7.04±0.5	7	79	4.49
50% DMF	25	1.00±0.02[d]			0.99±0.02			1.03
	30.3	1.02±0.02	3	30	1.02±0.03	6	57	1.0
	35.3	1.22±0.05	3	30				
	45.3	1.70±0.05	3	30	1.65±0.05	3	30	1.03
	65.5	2.95±0.17	3	20	3.03±0.05	3	20	0.98

a - Volume per cent

b - From ref.[6]

d - Interpolated from the Arrhenius equation

c - From ref.[7]

From Table 1 one can see that the rate constants values for phenylnitromethane with hydroxide ion in water measured by us, are in good agreement with those obtained by Munderloh[6].

The acceleration of proton transfer, observed due to the organic solvent component, is somewhat lower for phenylnitromethane than in case of nitroethane (11 and 13 fold in 50 vol % DMSO). However, the accelerating effect for deutero--phenyl-nitromethane is always higher than for proto-compound (11 and 33 fold in 50 vol % DMSO, 88 and 181 fold in 66.67 vol % DMSO), causing the decrease of the value of primary isotope effect observed. For the dissociation of phenylnitromethane in presence of NaOH in aqueous dimethyl formamide the value of isotope effect is practically equal to that of similar process for nitroethane ($k^H/k^D \approx 1$).

The activation parameters obtained in this study calculated according to the Arrhenius equation and activation parameters according to Eiring's equation and some data extracted from ref. 6 and 7, are collected in tables 2 and 3.

Table 2.

Parameters of Arrhenius Equation for the Reaction of Phenylnitromethane and Phenylnitromethane-d_2 with Hydroxide Ion in Aqueous DMSO and Aqueous DMF at 25°C. The standard deviations are listed.

Solvent[a]	Mol % of DMSO or DMF	E_a^H	E_a^D	lg A^H	lg A^D
50% DMSO	20.21	-	11.0±0.3	-	10.8±0.2
66.67% DMSO	33.63	-	7.1±0.3	-	8.7±0.2
50% DMF	18.9	6.1±0.2	6.1±0.2	7.4±0.1	7.4±0.1

a - Volume per cent

Table 3.

Parameters of Eiring's Equation for the Reaction of Phenylnitromethane and Phenylnitromethane-d_2 by Hydroxide Ion in Aqueous DMSO and Aqueous DMF

Solvent[a]	Mol % of DMSO or DMF	$\Delta H^{\neq}_H$	$\Delta H^{\neq}_D$	$\Delta S^{\neq}_H$	$\Delta S^{\neq}_D$
H_2O[b]	0	11.6	13.3	-9.4	-7.9
33.33% DMSO	11.24	9.2[c]	-	-15.5[c]	-
50% DMSO	20.21	8.3[c]	10.4	-15.8[c]	-11.2
66.67% DMSO	33.63	7.2[c]	6.5	-15.6[c]	-20.6
50% DMF	18.9	5.5	5.5	-26.9	-26.9

a - Volume per cent
b - From ref.[6]
c - From ref.[7]

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ELECTRON EFFECTS IN THE CHLORINE-CONTAINING HETEROCYCLIC COMPOUNDS. 1.AMINO-DERIVATIVES OF THE 2,4,6-TRICHLORO-1,3,5-TRIAZINE

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On the basis of the comparison of the obtained data on NQR ^{35}Cl frequencies, asymmetry parameters of the electric field gradient, the electron effects in aminoderivatives of the 2,4,6-trichloro-1,3,5-triazine have been investigated. Some regularities of the change in the C-Cl bond ionicity under the action of the inductive influence of the substituents have been established. Electronic conductivity of the triazine and benzene rings has been compared.

The reactivity of the 2,4,6-trichloro-1,3,5-triazine and its derivatives is determined both by the specificity of cyclic structure which formally resembles benzene, and by the nature of the functional groups. The presence of the three lone electron pairs at the nitrogen atoms and donor or acceptor substituents causes a significant rearrangement of the electronic system in these compounds and results, correspondingly, in a different chemical activity. In considered case, the transmission of the electronic influence of the amino-groups in the triazine ring, according to the NQR data at the ^{35}Cl nucleuses was investigated.

Up to now, the NQR frequency change regularities of the aromatic compounds have been investigated in detail. So, in in Refs. 1,2 the relationship between NQR frequencies and the constants, characterizing the nature of the substituents has been found, the quantitative evaluation of the aromatic ring transmission conductivity has been carried out.

II

The authors of the works[3,4] tried to extend these correlative relationships to the heterocyclic systems by introducing the corrections, considering the change of the double-bond character of the carbon-halogen bond and the influence of the heteroatoms. In the triazine series we investigated the NQR ^{35}Cl frequencies and the asymmetry parameters of the electric field gradient which allowed to make (according to Townes-Dayly theory) the estimation of the ionicity of C-Cl bonds as well as the degree of its double bonds character (5). In the considered structures it was possible that the ring geometry in varying amino-groups is maintained constant and the system of the main axises of the electric field gradient tensor for the halogen is maintained tightly fixed and the intramolecular interactions, affecting the parameter of the asymmetry, do not change the direction of the maximum electric field gradient. Only in this case we could expect, that the constants of the quadrupole interactions would be proportional to the values of the reaction substituent constants.

Experimental.

Amino-derivatives of 2,4,6-trichloro-1,3,5-triazine were synthesized according to the procedures [6-9]. The values of the electric field gradient asymmetry parameters were determined from the Fourier-image of the spin echo envelope in magnetic field on the ^{35}Cl nuclei[10,11]. Experimental values of the NQR frequencies (ν^{77}) and η were obtained at a modified spectrometer NQR IS-3 in the polycrystalline samples at temperature 77K.

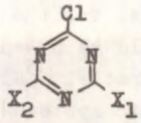
Estimates were carried out according to the develpped programs[10] at a "Nicolet" computer BNC-12. The measurement results of the defined values, the quadrupole interaction constants (eQq) and its ionicity (I) are summarized in the table.

For the structures 1-7,14 the spectrum multiplicity exceeded the number of the chemically inequivalent chlorine atoms in the molecule, indicating on the presence of two crystallographically independent molecules in the unit cell.

Breaking up values didn't exceed 1%. Subsequently the average frequency values ν will be used for these compounds.

Table

^{35}Cl NQR data of 2,4,6-trichloro-1,3,5-triazine derivatives



N	X_1	X_2	ν^{77}, MHz	eQq, MHz	η, (%)	I, (%)
1*	Cl	Cl	36.7708 36.7384	74.131 74.067	22 ± 1	10.2
2	Cl	NHMe	35.839 35.459	72.708 71.343	19 ± 2	14.3
3	Cl	NHEt	35.549 35.384	71.547 71.215	19.5 ± 1	14.5
4	Cl	NHi-Pr	35.536 35.165	71.476 70.730	18.5 ± 1	15.2
5	Cl	$N(Me)_2$	35.529 35.457	71.416 71.271	17.4 ± 1	15.4
6	Cl	$N(Et)_2$	34.875	70.155	18.7 ± 1	16.3
7	Cl	NC_5H_{10}	35.307 35.080	71.613 70.555	18.4 ± 1	15.5
8	NHMe	NHMe	33.900	67.99	13 ± 2	21.1
9	NHMe	NHi-Pr	33.660	67.682	18 ± 2	19.5
10	NHEt	NHEt	33.713	67.678	15 ± 2	20.7
11	NHEt	NHi-Pr	34.124	68.455	13.5 ± 1.5	20.4
12	NHi-Pr	NHi-Pr	34.216	-	-	-
13	$N(Me)_2$	$N(Me)_2$	33.884 33.747 33.318	68.035 67.760 66.900	15.4 ± 3	20.6
14	$N(Et)_2$	$N(Et)_2$	33.708	67.751	17.3 ± 2	19.7
15	NC_5H_{10}	NC_5H_{10}	33.611	67.638	19.3 ± 3	19.1

* The frequencies are given according to (5).

Results and Discussion.

The wide range of the frequency change (~ 3 MHz) while transforming from the original 2,4,6-trichloro-1,3,5--triazine (compound 1) disubstituted products, substantially exceeding the frequency interval for the benzene derivatives with similar substituents should be noted. The values of the asymmetry parameter on the nuclei ^{35}Cl indicate the greater (in comparison with aromatic systems) degree of the double-bonding carbon-halogen that was related, apparently, to the greater π-acceptor ability of the triazine ring. Introducing one or, especially, two electron-donating amino-groups results in the reduction of the π-acceptor cycle capacity and in the reduction of the degree of chlorine atom double-bond character. However, in some cases (see structures 9, 15), the observed great values of the parameter η , can be related to steric perturbation of the interaction of the lone pairs of the nitrogencontaining functional groups with triazine-ring, bound with them. The principle possibility of the use of Hammet meta σ constants in studying the influence of substituents structure on the rate of sym.- triazines hydrolyses has been established in a number of works[12, 13].

We also made an attempt to correlate the NQR frequencies with Hammet constants. The regression treatment of the average values ν and σ_m indicated, that only the rough linear relation for the considered series of the derivatives is observed:

$$\nu(\text{MHz}) = 34.799 + 2.358\ \sigma_m \quad (r=0.923) \qquad (I)$$

permitting, however, a decision to be made concerning the greater (then in aromatic systems) electron effects of the substituents on the chlorine atom frequency.

It is in accordance with the results of the works[12,13] in which higher heterocyclic transmission was observed. While analyzing NQR frequencies for the polysubstituted azines in the work[3] it was indicated, that the electron interactions in heterocycles could be quantitatively characterized by a two-parameter correlation[14] in the single reaction series with the benzene derivatives. The deviations from such relation observed for the compounds with hetero-

atom in α-position to the bond C-Cl, were eliminated by introducing the effective inductive parameters $\sigma_{I\ eff.}$ of the heteroatomic grouping -N= which, furthermore, became dependent on the number of adjacent nitrogen atoms. The application of $\sigma_{I\ eff.}$ for the series of sym.-triazines showed[3] great differences between calculated and experimental values of the NQR frequencies, exceeding -0.65 MHz in the case of compound I and +I MHz for compounds 8, 9, 10, 14, 15.

An alternative approach to the heterocyclic systems based on the use of the modified equation has been shown (4):

$$\nu\ (\text{MHz}) = 34.826 + 1.024\Sigma\sigma - \Delta\nu \qquad (2)$$

where $\Delta\nu$ accounts for the change of the C-Cl double-bond character due to the heteroatom influence. The comparison of the equations (1) and (2) indicates that in this case $\Delta\nu$ must increase in transferring from the trichlorotriazine to the disubstituted derivatives, which does not correspond to the observed character of the asymmetry parameter change. This fact indicates the inapplicability of such an approach to the given compounds. A more established fact, according to the Townes-Dayly theory, is the account of the asymmetry parameters in the calculation of the bond ionicity (I) which can be compared with the substituent inductive constants since the latter are in the m-position to the reactive center.

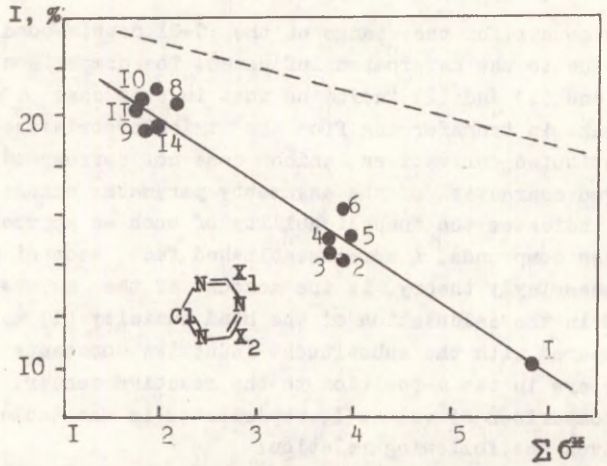
The comparison of values I, represented in the table, with σ^* gives the following relation:

$$I(\%) = 25.51 - 2.66\Sigma\sigma^* \ (r=0.977) \qquad (3)$$

The correlation equation has been derived from the data for 12 compounds. The following substituent constants were used: $\sigma^*_{Cl} = 2.89$; $\sigma^*_{N(Me)_2} = 1.1$ (16); $\sigma^*_{NHMe} = 1.018$ (17); $\sigma^*_{NHi\text{-}Pr} = 0.899$; $\sigma^*_{N(Et)_2} = 1.0$ (18). For the comparison of the C-Cl bond ionicity change dependence under the effect of the inductive influence in the aromatic compounds and in the triazine series the similar equation for the monochlorobenzene derivatives having the substituents in 3- and 5-positions has been found: $I(\%) \sim 23 - 0.65\Sigma\sigma^*$ (4)

In deriving this equation the experimental NQR frequency data were used, and the values of the asymmetry parameters were calculated according to the correlation equation, obtained as the result of the absence of values for the required number of the substituted aromatic compounds in the literature available.

Although eq. (4) has only the estimation character, the comparison of the induction members in (3) and (4) indicates that the substituents in the triazene ring have greater influence on the C-Cl bond ionicity than in the benzene ring.



Correlation between C-Cl bond ionicity and the reaction σ^*-Taft constants of substituents for the number of 2,4,6-trichloro-sym.triazine derivatives (equation 3); for comparison, dependence 4 is shown by the dotted line.

Consenquently, the research of the aminoderivatives of 2,4,6-trichloro-1,3,5-triazine by the NQR method made it possible to establish the regularities of the C-Cl bond ionicity change in the considered series under the action of the inductive substituents influence. The higher electron transmission and π-acceptor ability of heterocycle in comparison with the benzene ring have been observed.

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STUDY OF REACTIVITY OF SUBSTITUTED BICYCLO [2.2.2] OCTANES. 4. SELECTIVE DEOXYGENATION OF DIETHYL-2,5--DIOXOBICYCLO [2.2.2.] OCTANE-1,4-DICARBOXYLATE.

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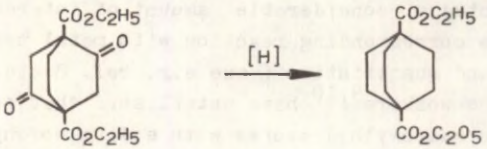
Literature methods for selective deoxygenation of diethyl-2,5-dioxobicyclo [2.2.2] octane-1,4- dicarboxylate (I) are verified and specified.

The degree of purity of product obtained by various methods of deoxygenation was checked by gasliquid (GLC) chromatography.

Conversion of tosylhydrazone (I) into the corresponding saturated diester II by sodium borohydride in dimethylformamide (DMF) was also attempted.

The reductive deoxygenation of carbonyl functions of diethyl-2,5-dioxobicyclo [2.2.2] octane - 1,4 - dicarboxylate (I) (see the scheme) is of considerable importance in the area of synthesis of bicyclo [2.2.2] octane derivatives.



I II

The classical procedures which are employed for converting ketones into the corresponding hydrocarbons often suffer from experimental difficulties and lack of selectivity. Likewise they work poorly and unpredictably when applied to sterically hindered carbonyl compounds.

Various Wolff-Kishner modifications have found considerable utility for deoxygenations but the high concentration of base and relatively vigorous conditions caused the failure in this case[1,2].

Traditional Clemmensen procedure is applied for deoxygenation of I in some different solvents. In toluene- water mixture the 2,5-dioxobicyclo [2.2.2] octane - 1,4 - dicarboxylic acid was gotten at 30 per cent yield[3]. Using dry ethanol and more diluted reagents the yield of diester II in 40 per cent was obtained.[4] 67 per cent yield of diester was realized by Wilcox[5] but he did not give full details of the synthesis and no analysis of the reduction product.

To carry out Clemmensen reaction, the prolonged refluxing under highly acidic reaction conditions is required and several side reactions can be assumed.

A rout is available for the synthesis of the desired bicyclooctane diester II through the thioketal formation from I and subsequent desulfurization with Raney nickel to the II, but it requires the use of large quantities of ethanedithiol and of Raney nickel[6,7].

Thus, investigation of the alternate procedures not requiring the use of these reagents is desirable.

The use of various metal hydrides as selective reducing agents has attracted a considerable amount of interest in recent years. The corresponding reaction with metal hydrides is often rapid and quantitative (see e.g. ref. 8 etc.).

Caglioti and coworkers[9,10] have established that reduction of p-toluene sulfonylhydrazones with sodium borohydride in refluxing methanol or dioxane effects the conversion of carbonyl compound to the corresponding hydrocarbon in reasonable yields (i.e.,30-80%) in many cases.However,the selectivity of sodium borohydride is not high at the required re-

duction temperatures (refluxing methanol or dioxane).

Sodium borohydride in polar aprotic solvents has proven to serve as a selective but somewhat milder reducing agent.[9,11]

It is of interest to obtain II by several routes of synthesis.

Special attention was paid to the conversion of tosylhydrazon of I to the corresponding saturated diester II by sodium borohydride in polar aprotic solvents.

Experimental.

All of the materials were either commercial products (purified) or synthesized by standard procedures. In all cases the physical constants agreed satisfactorily with the constants available in the literature.

GLC analyses were performed on a "Vibruchrom"-A-1 instrument using 3mx2mm XE-60(5%) column at 200°C. The retention times were compared with authentic samples. The yields were measured by comparing the peak area of the reaction product with the peak area of a standard solution of the same material.

1. Clemmensen Reduction of Diethyl-2,5-Dioxobicyclo-[2.2.2]octane-1,4-dicarboxylate (I).

Reduction of I by Clemmensen was carried out as described by Humber et al. (see ref. 4). The viscous liquid was obtained in overall yield 59-65%, b.p.143-146°C (3 torr) and n_D^{26}= 1.4725 (lit.b.p. 118-126° (0.3 torr), n_D^{26}= = 1.4628[4]; b.p. 140-145°(3 torr), n_D^{30}= 1.4723[3]; b.p. 113--115°(0.3 torr); n_D^{26}= 1.4660[6].

GLC detected 5-6 peaks. The second peak had retention time of II and was estimated in 30% yield.

On the bases of Wilcox's work[5] the mole ratio of zinc and I were varied from 20:1 to 7:1, but no essential differences were detected in the yields and product compositions.

2. Reduction by Raney Nickel Desulphurization of the Bisethylenethioketal Derivative of the Diketo--Diester of I

Ethanedithiol was prepared by the standard procedure.[12]

Bisethylenethioketal of I was prepared by the procedure of Roberts[6] and had mp. 88-89°C (lit.[7] mp. 92°C).

Alloy of Raney Nickel (Nickel containing 44%) was worked up until neutral to litmus in accordance with instruction [13]. After treating the catalyst with 2-3 portion of dry ethanol, it was immediately utilized in reduction procedure. Replacing 95 per cent with dry ethanol reduction was realized according to Roberts[6]. The yield 85-95 per cent was obtained, b.p. 144-146°C (3 torr), n_D^{25}= 1.4663. GLC showed only one component. Lit.[6] yield 52-70 per cent, b.p. 113-115 (0.3 torr), n_D^{26}= 1.4660.

3. Attempt to Convert Tosylhydrazone of I to the Corresponding Saturated Diester II by Sodium Borohydride in DMF

p-Toluenesulfonylhydrazine was prepared by the standard procedure[14], m.p. 107-109, lit.[14] m.p. 106-109°C.

Tosylhydrazone of I (TH) was prepared by analogical method.[11]

1.7 g diketone I and 2.9 g p-toluenesulfonylhydrazine in 5 ml of absolute ethanol were refluxed for 8 h.Cooling of the solutions afforded crystalline product in excellent yields (94-96 per cent),m.p. 225-227°C. The product was usually pure enough and further recrystallization was not necessary for the reduction step. An analytical sample of TH crystallized from ethanol, m.p. 228-229°C.

Anal. calcd. for $C_{28}H_{34}O_8N_4S_2$: C, 54.35; H, 5.54; N, 9.06. Found: C, 53.91; H, 5.35; N, 9.11.

Reduction of Tosylhydrazone of I (TH) with Sodium borohydrine in DMF.

To a stirred solution of 0.9 g TH (entry 4) in 50 ml dry DMF was added $NaBH_4$ 2 g during an hour. Stirring was continued for 48 h at room temperature and 10 h at 60°.The

mixture was cooled and neutralized with 10 per cent HCl and extracted with ether. The extracts were washed with water and dried over anhydrous magnesium sulfate. Analysis indicated 10-12 per cent saturated ester II, free of side products.

Acidification (entry 5) was carried out by adding concentrated HCl dropwise through the top of the condenser to keep pH below 3.8 (the pH value was controlled by universal indicator paper). Work-up was identical with that given above.

In order to establish optimum reaction conditions for reduction in DMF, the concentration of $NaBH_4$ and TH and temperature were varied. The most successful mole ratio of $NaBH_4$ to TH was found to be 30:1. The data are presented in Table 1.

Some other solvent systems including dimethyl sulfoxide, diglyme and 80 % diglyme-H_2O were also tested without success.

The use of $NaBH_4$ in carboxylic acid solvents (CH_3CO_2H) suggested by ref. 15, 16 in this case failed.

Table 1

Reduction of Tosylhydrazone of I (TH) with Sodium Borohydride in Dimethylformamide (DMF)

Entry	TH:$NaBH_4$	pH	Reaction Conditions Temp.°C/time (h)	Yield %	Notes
1.	1:8	8	50 / 30	-	
2.	1:20	8	20 / 12 60 / 6	-	
3.	1:20	8	100 / 5	-	form thick gel
4.	1:30	8	20 / 48 60 / 10 20 / 2	10 - 12	
5.	1:30	3.8	60 / 3	3 - 4	
6.	1:30	8	60 / 24	10	form gel

Summary.

The experimental data available indicates that the high--yield (85-95 per cent) method for deoxygenation of diketodiester I is desulfurization its thioketal with Raney nickel. The product obtained was clean, no side products were detected by CLC.

Clemmensen reduction procedure gave low yields of impure material.

Reduction of tosylhydrazone of diketodiester I with sodium borohydride in polar aprotic solvents to the corresponding saturated diester II is not recommended as a method for synthetic applications. Although the tosylhydrazone of I is produced in excellent yield (94-96 per cent), the subsequent reduction of tosylhydrazone with sodium borohydride is slow (yield 10-12 per cent).

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STUDY OF REACTIVITY OF SUBSTITUTED BICYCLO [2.2.2] OCTANES. 5. CYCLOADDITION REACTION BETWEEN ETHYL--1,3-CYCLOHEXADIENE-1-CARBOXYLATE AND NITROETHYLENE .

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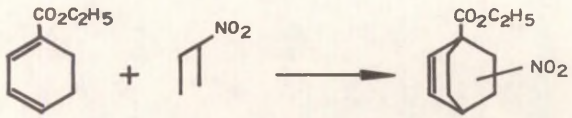
The cycloaddition reaction between ethyl-1,3-cyclohexadiene-1-carboxylate (I) and nitroethylene (II) in dry benzene (and without solvent) was studied. The adduct (III) was formed in 66--92 per cent yield, b.p. 122°C/1-2 mm. The product was characterized by IR spectra.

Most probably the cycloaddition reaction of ethyl-1,3--cyclohexadiene-1-carboxylate with nitroethylene would be characterized by the scheme[1]:



I II III

Activated by conjugation, nitroethylene should be the most active of the monofunctionalized acrylic dienophiles in Diels-Alder reaction (see Ref. 2-3, etc.).

The yield of expected Diels-Alder adduct is decreased by easy polymer formation of nitroethylene.[4] It polymerizes readily with water and violently in the presence of a trace

of alkali.

To avoid polymerization, generation of nitroethylene in situ for use of Diels-Alder reaction is described[5].

Since nitroethylene holds promise as a useful and reactive synthon in organic syntheses, the question of its stabilization was examined several times (see Ref. 6, 7, etc.).

Recently it has been pointed out[3,7] that with reactive substrates nitroethylene reacts most easily at low temperature and when stored as a 10% solution in benzene in refrigerator (+10°C), it is stable for at least 6 months. Whereas there are no literature reports on the above-mentioned cycloaddition reaction, the purpose of this work is to study and specify the optimum conditions of diene condensation of ethyl 1,3-cyclohexadienecarboxylate with nitroethylene.

Experimental

Infrared spectra were performed on a "IKS-29" spectrometer

Ethyl-1,3-cyclohexadiene-1-carboxylate (I) was synthesized by the procedure of Grob and Ohta[8] (see also Ref.9).

2-nitroethanol was prepared from formaldehyde and nitromethane[10]. The constants were in good accordance with the literature values.

Nitroethylene (II) was synthesized by the procedure of phthalic anhydride mediated dehydration of 2-nitroethanol[4], it was several times dried over anhydrous $MgSO_4$, distilled in vacuum, b.p. 38-39°C/80 mm Hg and stored as a 10 per cent solution in dry benzene at +10°C.

Generation of Nitroethylene (II) in situ for use in Diels-Alder Reaction with Ethyl 1,3-cyclohexadiene-1-carboxylate (I) was carried out by analogy[5].

Ethyl-1,3-cyclohexadiene-1-carboxylate (2 g 0.013 mol), 2-nitroethanol (2.28 g, 0.025 mol), phthalic anhydride (3.70g, 0.025 mol), and hydroquinone (2.75 g, 0.025 mol) were placed in tube. The tube was flushed with argon, sealed, and heated for 30 minute at 100-120°C. Then the temperature was increased to 140-150°C and heated at this temperature for 24 h. After cooling down the mixture was extracted with benzene. The benzene extracts were dried over $MgSO_4$, and the removal of

the solvent in vacuo gave crude product as yellow-white crystals, 0.33 g (11.2%), m.p. 160°-170°C (decomposition).

The synthesis was repeated by the above described procedure using benzene (4 mL) as solvent. For once 0.40 g (16%) of crystallic product was obtained, m.p. 160-170°C.By storing these yellowish-white crystals became dark.

A small sample was recrystallized from benzene and analyzed.

Anal. calcd for expected compound

$C_{11}H_{16}O_4N$: C, 58.39; H, 7.13; N, 6.19

Found : C, 35.38; H, 4.39; N,18.20

Calcd for

$(-CH=CNO_2-)_2$ C, 32.43; H, 5.44; N,18.90

The infrared spectrum (oil) has band at 1555 cm^{-1} (NO_2).

Cycloaddition Reaction of Ethyl-1,3-cyclohexadiene-1-carboxylate (I) with nitroethylene (II).

Nitroethylene was synthesized[4], carefully dried and distilled in vacuo. Immediately after distillation II was diluted with dry benzene and stored as 10 per cent solution at +10°C.

In the runs 1 and 2 there was the fresh-made nitroethylene used.

Representative Examples(see run 7, Table 1)

Under argon atmosphere a solution of nitroethylene (2.17g, 0.029 mol) in dry benzene (24 mL) was added dropwise during 6 h at 80°C to ethyl-1,3-cyclohexadiene-1-carboxylate (3.7 g, 0.024 mol) and refluxed for 18 h at this temperature.The solvent was evaporated in vacuo and the residue vacuum distilled. A pale yellow oil was gotten, b.p. 122°C/1-2 mm. Yield $\geqslant$ 62% . In distillation and at storing the product fast became dark.

In connection with the decomposition of III, the yield was calculated a) by the unreacted and distilled diene I (b.p.$\leqslant$75°C/1-2 mm) b) by distilled product III (b.p.122° C/ /1-2 mm). Run 8 (see Table 1). This synthesis was carried out by analogy to Run 7.The mixture was refluxed at 80°C. After that benzene was evaporated in vacuo and product III was hydrogenated on PtO_2 in the atmosphere of hydrogen (at atmos-

Table 1

Data on the Cycloaddition Reaction of Ethyl-1,3-Cyclohexadiene-1-carboxylate (I) with Nitroethylene (II).

No	Amount of diene I and dienophile II in g (in moles)	Reaction conditions			Yield of III, %		Notes
		Solvent	Temp. °C	Time h	a)	b)	
1.	1.6(0.010)I 1.0(0.013)II	-	room	48	-	-	50% of polymeric product
2.	1.6(0.010)I 1.0(0.013)II	-	100	1	-	-	Decomposition, the brown gases are separated
3.	1.6(0.010)I 1.0(0.013)II	67% in benzene	room	26	-	-	40% of polymeric product
4.	1.6(0.010)I 1.0(0.013)II	10% in benzene	room	3 month	74	33	Rich dark precipitate in distillation is formed
5.	1.6(0.010)I 1.0(0.013)II	- " -	80	11	64	34	- " -
6.	2.5(0.025)I 2.0(0.027)II	- " -	80	18	71	48	- " -
7.	3.7(0.024)I 2.2(0.029)II	- " -	80	24	90	62	- " -
8.	3.3(0.021)I 2.0(0.027)II	- " -	80	30			Product III is hydrogenated on PtO_2 and distilled, yield 66%
9.	1.6(0.010)I 1.0(0.013)II	-" -	100	18	87	49	Rich dark precipitate in distillation is formed

a) The yield was calculated by nonreacted diene

b) The yield was calculated by distilled product III.

pheric pressure). After the filtration of the catalyst, the saturated product was vacuum distilled, b.p. 125-127°C/1-2mm, in yield 66%. The product has typical smell of bicyclo [2.2.2] octane carboxylic acid esters.

The infrared spectrum (KBr) has bands at 853 (NO_2); 1070--1250 (C-O); 1340, 1555 (NO_2), 1730 (C=O); 2880, 2940, 2985 (CH_2) CM^{-1}.

Table 1 summarizes the data on synthesis.

Discussion.

From the data obtained one can see that the yield of Diels-Alder adduct is decreased by polymerization of nitroethylene (see Table 1, entry 1-3). Most suitable is to carry out the cycloaddition reaction of nitroethylene with I in dry benzene using 10 per cent nitroethylene solution. The optimum temperature for the synthesis is 80°C. The heating for 24 h in anhydrous argon atmosphere results in the adduct, pale yellow oil, b.p. 122°/1-2 mm Hg. Its partial decomposition takes place in distillation. When preserved the pale yellow oil fast becomes dark.

The yield calculated by unreacted diene I is 90 per cent, by the distilled adduct III -- 62 per cent, only.

Products III hydrogenation was undertaken without intermediate distillation to avoid its decomposition (see entry 8, Table 1)

IR spectrum of hydrogenated product showed the bands attributed to the nitro- and ester groups.

This saturated nitrobicyclo [2.2.2] octane carboxylic acid ester is more stable than III.

In cycloaddition reaction with generation of nitroethylene in situ the polynitroethylene was obtained only.

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STUDY OF REACTIVITY OF SUBSTITUTED BICYCLO [2.2.2] OCTANES. 6. ABOUT CYCLOADDITION REACTION BETWEEN SOME 1,3-CYCLOHEXADIENS AND MONOFUNCTIONAL ETHYLENES

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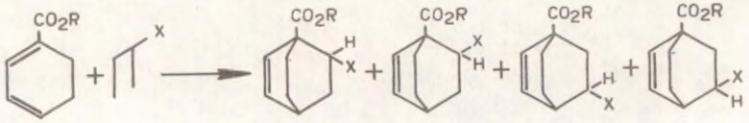
The literature reports and the data about cycloaddition reaction between some 1,3-cyclohexadiens and various monofunctional XCH = CH_2 (X = NO_2, CN, CHO, $COCH_3$, $CO_2C_2H_5$ and CO_2H) ethylenes (i.e.acrylic dienophiles) gathered in our laboratory are discussed. The reaction conditions and total yield dependence on the nature of dienophiles are discussed.

To obtain 1-Y-2-X and 1-Y-3-X bicyclo [2.2.2] octane derivatives, where Y = CO_2HCO_2R and X = NO_2, CN, CHO, $COCH_3$, $CO_2C_2H_5$ and CO_2H the cycloaddition reaction with subsequent hydrogenation of adduct is most often used.

In cycloaddition reaction of 1,3-cyclohexadiene or ethyl--1,3-cyclohexadiene with acrylic dienophiles the bicyclo [2.2.2] octane skeleton will be formed. Usually, the adduct represents a mixture of four isomers (see the scheme).



Determination of relative yields of these isomers was the aim of some investigations (see Ref. 1-2, etc.).

At room temperature 1,3-cyclohexadiene reacted with several dienophiles rapidly and quantitatively, but with acrylic dienophiles heating is usually necessary. (See Table 1).

By heating the thermally stable dimers of 1,3-cyclohexadien are formed and simultaneous polymerization of acrylic dienophiles takes place lowering the yield of Diels-Alder adduct.[3]

The rate cycloaddition reaction of cyclohexadiene with acrylic dienophiles depends on the nature of diene and dienophile. Thus, ethylene reacts with 1,3-cyclohexadiene only at vigorous conditions (see Table 1). Strongly activated dienophiles such as nitroethylene, acrylonitrile, etc. react more easily.

Diels-Alder reactivity of 1,3-cyclohexadiene and substituted cyclohexadienes with acrylic dienophiles are not examined in detail. Literature data about the series are scanty.

To carry out cycloaddition reaction of 1,3-cyclohexadiene and substituted cyclohexadienes with acrylic dienophiles heating, either in flask with reflux condenser or in sealed ampules at various temperatures, is used (see Table 1 and 2).

In utilization of cycloaddition reaction for preparation of 1-Y-2-X and 1-Y-3-X derivatives of bicyclo [2.2.2] octane the total yield of this stage has essential practical importance.

In the present paper based on the literature reports and our experimental data an attempt is made to draw a connection between Diels-Alder reaction conditions and total yield dependences on the nature of acrylic dienophiles.

Experimental

Ethyl-1,3-cyclohexadiene carboxylate was synthesized by the procedure of Grob and Ohta[14] (see also Ref. 10).

Dienophiles I - III and VI ("Pure for analysis" grade) were dried carefully by standard procedures and used freshly distilled only.

Nitroethylene (V) was synthesized by the procedure of

Table 1

Data on the Cycloaddition Reaction of 1,3-cyclohexadiene with Monofunctional Ethylenes XCH = CH_2; Procedure A, Heating in the Sealed Ampule. Procedure B, Heating with Reflux Condenser

No	X in dienophile	Reaction conditions	Yield, %	
		Procedure, temp., time		Ref.
	H	pressure, 250°C, 24 h, 50 atm	56	4
I	$CO_2C_2H_5$	Proc.A, 160-170°C, 12 h	88	5
II	CN	Proc.B, 120°C	80	6
III	CHO	Proc.A, 100°C, 8 h	80	7
IV	$COCH_3$	Proc.A, 140°C, 8-10 h	50	8
V	NO_2	Proc.B, heating, 1 h	33	9

phtalic anhydride mediated dehydration of 2-nitroethanol[15] (see Ref. 16).

Procedure A for cycloaddition reaction

0.023 mol diene, 0.092 mol dienophile and 0.04 hydroquinone were placed in a glass ampule, flushed with dry argon and sealed. The sealed ampule was heated at 140°C for 24 h. The reaction mixture occupied 1/3 to 1/2 of the tube volume.

Adducts I-III were distilled in vacuum and analyzed. In all cases the physical constants agreed satisfactorily with the constants available in the literature.

GLC analysis were performed at a "Vöruchrom"-A-1 instrument, using 3x2 mm XE-60 (5%) column at 200°C.

According to the GLC procedure adducts I-III contain four isomers whose total yield was calculated.

In cycloaddition reaction with dienophile VI 1,2-dicarboxylic acid of bicyclo [2.2.2] octane was obtained. After recrystallizing the product from benzene the white crystallic product (m.p. 202-203°C (lit.[1] 202-204) was obtained.

Procedure C for cycloaddition reaction,

heating with reflux condenser in the atmosphere of anhydrous argon and in dry benzene as solvent was used in the case of

Table 2

Data on the Cycloaddition Reaction of Ethyl-1,3-Cyclohexadienecarboxylate with Monofunctional Ethylenes $XCH=CH_2$. For Dienophiles I-III Ratio of Dienophile--diene 4:1 for V and VI -- 1,2:1, Respectively

No	X in dienophile	This work*			Literature data			
		Reaction conditions		Yield,%	Reaction conditions		Yield,%	Ref.
I	$CO_2C_2H_5$	Proc.A	140°C 24 h	77 ± 3	Proc.B	120°C 24 h	50	1;10
II	CN	Proc.A	140°C 24 h	79 ± 2	Proc.A	170°C 9 h	73	11
III	CH	Proc.A	140°C 24 h	72 ± 2	Proc.B	150°C 90 h	47	12
IV	$COCH_3$				Proc.A	140°C 18 h	89	2
V	NO_2	Proc.C	80°C 24 h	76 ± 14				
VI	CO_2H	Proc.A	140°C 24 h	27 ± 2	Proc.B	150-160°C 78 h	24,8	13

* The yields are calculated as arithmetic mean of 2 to 4 synthesis

Procedure A, heating in the sealed ampule in the atmosphere of anhydrous argon

Procedure B, heating with reflux condenser

Procedure C, heating with reflux condenser in the atmosphere of anhydrous argon and in dry benzene as solvent.

dienophile V. After heating at 80°C for 24 h a pale yellow oil was achieved, b.p. 122°C/1-2 mm. (For details of this synthesis see Ref. 16).

Discussion

In order to establish qualitative dependence of dienophile reactivity, the cycloaddition reaction of ethyl-1,3--cyclohexadienecarboxylate with monosubstituted ethylenes

in similar experimental conditions were studied in the present paper.

Heating in sealed ampule for 24 h at 140°C was used with the only exception of nitroethylene which decomposes at these conditions.

From data represented in Table 2 one can see that adducts of cycloaddition of substituted 1,3 - cyclohexadiene with monofunctiolized ethylene, $XCH=CH_2$ at $X=CO_2C_2H_5$, CN, CHO in the similar experimental conditions were formed at a 70-80 per cent yield. Strongly activated dienophile such as nitroethylene ($X=NO_2$) reacts readily with diene. Unfortunately, nitroethylene's tendency to polymerize is high and cycloaddition reaction in this case was realized in the dry benzene at 80°C. During 24 h heating the yield from 62 to 90 per cent was got. The partial decomposition of adduct in distillation and storing did not allow to establish the yield more precisely. (See Ref. 16).

Less reactive was acrylic acid ($X=CO_2H$). At the same time only a 25 per cent yield was achieved.

By literature reports there are some other cases when the same ranging of Diels-Alder activity of acrylic dienophiles was found. Thus, with bensofuran[17] the rate decreasing line was the following: nitroethylene > acrylonitrile > > acrolein > methylvinylketone > acrylic acid.

Recently[18], the cycloaddition reaction of 1,4-diethoxy--1,3-cyclohexadiene with some monosubstituted ethylenes was studied and found that dienophilic reactivity decreases as follows:

nitroethylene > acrylonitrile > acrolein.

These results are in accordance with electronic characteristics of dienophiles - electron with drawing substituents facilitate the reaction. As compared with dienophiles the reversed substituent effect is present in the case of dienes. In its turn, 1,3-cyclohexadiene is somewhat more reactive than ethyl-1,3-cyclohexadiene carboxylate.

Consequently, the represented results about the reactivity of monofunctional ethylenes with some 1,3-hexadienes follow the regularities which generally apply to diene syn-

thesis.

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